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MATHÉMATIQUES

SUR LES TABLES OPTIMALES À TROIS MEMBRES DES FONCTIONS DE DEUX VARIABLES

Par L. NEUSCHULER

(Présenté par S. L. Soboleff, de l'Académie, le 8. VII. 1939)

Si l'on formait pour les fonctions de deux variables $f(x, y)$ une table ordinaire à l'entrée double, le volume de cette table, pour un nombre suffisamment élevé de valeurs que prennent les deux variables, sera si grand, qu'on peut considérer une telle table comme pratiquement irréalisable.

Dans la présente Note il est question des tables ayant le volume minimum*, formées pour les fonctions de deux variables et basées sur les procédés, excluant les opérations et ne comprenant que la lecture successive de trois résultats (chaque fois par deux valeurs, dans la colonne qui en contient l'une et dans ligne contenant l'autre) dont le troisième représente la valeur cherchée de la fonction.

Si l'on admet le procédé consistant en trois «lectures», on peut souvent arriver à la possibilité de restreindre considérablement ce volume et former de cette sorte les tables irréalisables par la méthode ordinaire à cause de leur dimension démesurée.

Appelons la table

x / y	$a_{11}\cdots$	a_{1r}	$\cdots a_{1m_1}$
b_{11}			
$\vdots$			
b_{1l}		Φ_{1rl}	
$\vdots$			
b_{1n_1}			

x / y	$a_{21}\cdots$	a_{2s}
b_{21}		
$\vdots$		
b_{2t}		Φ_{2st}
$\vdots$		
b_{2n_2}		

x / y	$a_{k1}\cdots$	a_{kp}	$\cdots a_{km_k}$
a_{2m_2} $\cdots b_{k_1}$			
$\vdots$			
$\cdots b_{kq}$		Φ_{kpq}	
$\vdots$			
$\cdots b_{kn_k}$			

table à un membre de $\Phi(x, y)$.

Désignons par volume d'une table (a) à un membre la somme

$$\sum_{i=1}^{k} m_i n_i.$$

On peut former pour une fonction d'une forme spéciale de deux variables

$$f(x, y) = F[\varphi_1(x) + \varphi_2(y)]$$

* Le volume est défini par le nombre de valeurs de la fonction, contenues dans la table.

une table, dont l'emploi n'exige pas d'additions et ne consiste qu'en trois «lectures» successives. Le volume de cette table sera souvent moindre que celui d'une table à un membre de $f(x, y)$.

En effet, considérons la suite des valeurs $z_1, z_2, \ldots, z_n$ et formons une table composée de trois tables à un membre (appelées dans la suite composantes) de trois fonctions suivantes:

1) $\varphi_1(z_i)+\varphi_2(y)$

2) $\varphi_1(x)-\varphi_1(z_i)$, où $z_i \leqslant x \leqslant z_{i+1}$, et

3) $F(u+T)$, où u prend la suite des valeurs comprises entre les valeurs maximum et minimum de $\varphi_1(z_i)+\varphi_2(y)$, dépendant de la table, et où T peut prendre la suite des diverses valeurs, de précision donnée, parcourues par $\varphi_1(x)-\varphi_1(z_i)$, lorsque $z_i \leqslant x \leqslant z_{i+1}$.

Le volume d'une telle table dépend par conséquent du choix de la suite des valeurs $z_1, z_2, \ldots z_n$, que nous appelerons base. La base, pour laquelle le volume de la table est minimum, sera appelée base optimum.

Les limites de variation de x et de y, ainsi que la précision étant données, on aura: 1) le volume de deux premières composantes ne dépend que du nombre de membres de la base; 2) le volume de la troisième composante est déterminé par le maximum de $\varphi_1(x)-\varphi_1(z_i)$.

Considérons deux telles tables, l'une formée pour une base quelconque $z_1, z_2, \ldots z_n$ et l'autre pour la base $x_1, x_2 \ldots x_m$, dont les membres vérifient l'égalité

$$\varphi_1(x_{i+1})-\varphi_1(x_i)=\max[\varphi_1(z_{j+1})-\varphi_1(z_j)].$$

Il est facile de voir que le volume total de toutes les trois composantes de la seconde table sera inférieur ou égal à celui de la première quelle que soit la suite $z_1, z_2 \ldots z_n$. Par conséquent, l'on a

Théorème 1. *Pour qu'une suite $z_1, z_2, \ldots z_n$ soit une base optimum d'une table de construction considérée et formée à partir de la fonction $F[\varphi_1(x)+\varphi_2(y)]$, il suffit que les membres de la base satisfassent à la condition*

$$\varphi_1(z_{i+1})-\varphi_1(z_i)=c \text{ (const)}.$$

Composons l'expression de la somme des volumes de toutes les trois composantes, qui sera évidemment une fonction $\mu(c)$. En déterminant la valeur de c, pour lequel $\mu(c)$ est minimum, nous pouvons définir les membres de la base optimum.

Plus haut nous avons examiné la question de la formation d'une table optimum (de volume minimum) pour une fonction spéciale $F[\varphi_1(x)+\varphi_2(y)]$, cette table comprenant: 1) les composantes $\varphi_1(z)+\varphi_2(y)$, 2) les composantes $\varphi_1(x)-\varphi_1(z)$, 3) les composantes dépendant de la somme des valeurs obtenues dans la première et la seconde composantes.

Considérons maintenant la question de possibilité de formation pour une fonction arbitraire $f(x, y)$ d'une table optimum, contenant trois composantes d'une forme plus générale: 1) $u=\varphi(z, y)=\eta[f(z, y)]$, 2) $T=\psi(x, z)$ et 3) $F(u, T)$, telles que pour tout $a_1 \leqslant x \leqslant b_1$ et $a_2 \leqslant y \leqslant b_2$ on a $|F(u, T)-f(x, y)| \leqslant \varepsilon$, à condition que $|u-\varphi(z, y)| \leqslant \delta_1(\varepsilon)$ et $|T-\psi(x, z)| \leqslant \delta_2(\varepsilon)$ et $f(x, y)=F(u, T)$, si $u=\varphi(z, y)$ et $T=\psi(x, z)$.

Appelons une telle table table à trois membres, et une fonction, pour laquelle une telle table peut être formée, fonction ayant une table à trois membres. Dans la suite il sera question des tables à trois membres.

Fonction ψ sera appelée fonction rétablissante de $f(x, y)$.

Pour que l'identité

$$F[f_1(x, y, z), \quad f_2(x, y, z), \quad f_3(x, y, z)] \equiv 0$$

subsiste, il est suffisant et nécessaire que la jacobienne correspondante soit identiquement nulle. Il en suit

Lemme 1. *Pour qu'on puisse former une table de $f(x, y)$ ayant les dérivées partielles du 1-er et du 2-me ordre prises par rapport aux deux variables, les dérivées partielles du premier ordre n'étant pas identiquement nulles, il est nécessaire et suffisant que l'on ait*

$$\frac{\partial R}{\partial y} = 0, \quad où \quad R = \frac{\partial f(x, y)}{\partial x} \frac{\partial f(z, y)}{\partial y} : \frac{\partial f(x, y)}{\partial y} \frac{\partial f(z, y)}{\partial z}.$$

La condition est suffisante, car étant remplie $R(x, z)$ représente le rapport de la forme $\frac{\psi_1(x)}{\psi_2(z)}$ et, si l'on prend

$$\psi = \Phi\left[\int \psi_1(x)\, \partial x - \int \psi_2(z)\, dz\right],$$

la jacobienne correspondante serait nulle.

Il est facile de voir qu'il suit du lemme 1, que $\frac{\partial f}{\partial x} : \frac{\partial f}{\partial y}$ représente le rapport de la forme $\frac{f_1(x)}{f_2(x)}$. D'où l'on a

Théorème 2. *Pour que $f(x, y)$ ait une table à trois membres, il est suffisant et nécessaire que l'on ait l'identité*

$$f(x, y) \equiv F[\varphi_1(x) + \varphi_2(y)]. \tag{A}$$

Comme la jacobienne, d'après le lemme 1, est nulle, on peut aussi trouver la fonction rétablissante d'après le théorème 1.

En effet, si $f(x, y) \equiv F[\varphi_1(x) + \varphi_2(y)]$, et en tenant compte du lemme 1, ψ satisfait à l'équation $\frac{\partial \psi^*}{\partial x} + \frac{\partial \psi^*}{\partial z} \frac{\varphi_1'(x)}{\varphi_1'(z)} = 0$ et la fonction rétablissante est de la forme $F^*[\varphi_1(x) - \varphi_1(z)]$. D'après ce qui précède, l'on a

Lemme 2. *La subsistance de l'identité de la forme*

$$f(x, y) \equiv \Phi\{\Phi_1[\varphi_1(z) + \varphi_2(y)], \quad \Phi_2[\varphi_1(x) - \varphi_1(z)]\} \tag{B}$$

est la condition suffisante et nécessaire pour que la fonction $f(x, y)$ ait une table.

En tenant compte, que les volumes des tables optima des fonctions $f(x, y)$ et $F[f(x, y)]$ et les volumes des tables optima à un membre pour $F(u, T)$ et $F(u + T)$ sont égaux entre eux, on aura d'après les identités (A) et (B):

Théorème 3. *Si $f(x, y)$ est une fonction ayant une table à trois membres, la table présentant l'ensemble de trois tables à un membre*

1) $u = \varphi_1(z_i) + \varphi_2(y)$, 2) $T = \varphi_1(x) - \varphi_1(z)$, 3) $S = F(u + T)$

à condition que $z_i \leqslant x \leqslant z_{i+1}$, $|\varphi_1(z_{i+1}) - \varphi_1(z_i)| = c$, est optimum (la valeur c étant telle que le volume de la table $\mu(c)$ soit minimum), φ_1, φ_2 et F étant liés à $f(x, y)$ par une identité $f(x, y) \equiv F[\varphi_1(x) + \varphi_2(y)]$.

L'existence d'une table à trois membres pour la fonction $f(x, y)$ est basée sur l'existence de

$$f(x, y) \equiv F[f(z, y), \quad \varphi(x, z)]. \tag{α}$$

Il suit du lemme 1 qu'il résulte de (α)

$$f(z, y) \equiv F^*[f(z, u), \quad \psi(y, u)]. \tag{β}$$

On a d'après (α) et (β)

$$f(x, y) \equiv F\{F^*[f(z, u), \quad \psi(y, u)], \quad \varphi(x, z)\}$$

ce qui permet de former une table à cinq membres: 1) $x_1 = f(z, u)$, 2) $x_2 = \psi(y, v)$, 3) $x_3 = F^*(x, x_2)$, 4) $x_4 = \psi(x_1, z)$, 5) $x_5 = F(x_3, x_4)$.

Il en suit

Théorème 4. *Pour qu'il existe une table à cinq membres, il suffit qu'il existe une table à trois membres.*

On peut citer comme exemples de fonctions ayant des tables à trois, et par conséquent, à cinq membres, les fonctions suivantes:

$$f\left(xy + \frac{x}{y}\right), \quad F[f_1(x) f_2(y)], \quad F\left[\frac{f_1(x)}{f_2(y)}\right],$$

$$f(x^m + y^n) \quad \text{et} \quad F[f_1(x) f_2(y) a^{\varphi_1(x)+\varphi_2(y)}].$$

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PHYSIK

ZUR FRAGE ÜBER DIE CHEMISCHE NATUR DER PRODUKTE, WELCHE BEI DER TEILUNG DES URANKERNES UNTER EINWIRKUNG VON NEUTRONEN ENTSTEHEN. I*

Von V. G. CHLOPIN, Mitglied der Akademie, M. A. PASWIK-CHLOPIN und N. F. VOLKOV

Ein neuer Typus des Kernzerfalls der schweren Elemente—Urans und Thoriums—der unabhängig voneinander und fast gleichzeitig von O. Hahn und F. Strassmann (1), F. Joliot (2) und L. Meitner und O. Frisch (3) entdeckt wurde und der in einer Teilung des Kernes in zwei Bruchstücke von annähernd gleicher Masse zum Ausdruck tritt, veranlasst die Entstehung als Teilungsprodukte des Urans und des Thoriums einer ganzen Reihe von chemischen Elementen, die in der Mitte des Periodischen Systems stehen.

Ausgehend aus der Massendefektskurve haben F. Joliot einerseits und L. Meitner und O. Frisch andererseits zeigen können, dass die Teilung des Urankernes mit einer Energieausbeute von circa 150—200 MeV verbunden ist. Die bei einer solchen Teilung entstehenden Bruchstücke—Kerne leichterer chemischer Elemente—besitzen demgemäss bei ihrer Entstehung beträchtlich mehr Neutronen im Kerne, als es den stabilen Atomkernen von derselben Atomnummer entspricht.

Dem entsprechend sind die bei der Teilung des Urankernes sich bildende Kerne der leichteren chemischen Elemente bei ihrer Entstehung instabil und haben die Tendenz durch Abspaltung eines Teils der überschüssigen Neutronen einerseits, und durch eine Reihe von β-Umwandlungen, bei denen die Neutronen in Protonen übergehen, andererseits, in einen stabilen Zustand zu übergehen. Die theoretischen Überlegungen zeigen es, dass vom energetischen Standpunkte aus mehrere Teilungsschemata des Urankernes möglich und annähernd ebenso wahrscheinlich sind. Dieser Schluss findet experimentelle Bestätigung; dadurch soll auch die grosse Mannigfaltigkeit der chemischen Eigenschaften der bei der Spaltung des Urankernes entstehenden Produkte erklärt werden.

Drei verschiedene Teilungsschemata des Urankernes wurden solange vorgeschlagen:

1) $^{235}_{92}U + ^{1}_{0}n \rightarrow ^{236}_{92}U$; $^{236}_{92}U \rightarrow ^{141}_{55}Cs + ^{95}_{73}Rb$; (F. Joliot)

2) $^{236}_{92}U \rightarrow ^{143}_{56}Ba + ^{93}_{36}Kr$;

3) $^{236}_{92}U \rightarrow ^{139}_{54}X + ^{97}_{38}Sr$ (O. Hahn u. F. Strassmann; L. Meitner u. O. Frisch)

* Vorgetragen auf der Generalversammlung der Akademie d. 29. V. 1939.

Gemäss diesen drei Teilungsschemata sollte man unter den Teilungsprodukten des Urans das Auftreten von Elementen, welche zwischen Krypton und Yttrium, Zink oder Niobium, einerseits, und Xenon und Praseodymium oder Neodymium, andererseits, in dem Periodischen System stehen. Ausser diesen drei Teilungsschemata sind aber wahrscheinlich auch andere möglich. Darauf deutet unter anderem die Auffindung unter den Teilungsprodukten des Urans von Halogenen ([4-6],[9]), einerseits, und von Atimon und Tellur ([6],[7],[9]), andererseits; zu denselben Schlussfolgerungen führt auch die Untersuchung der chemischen Natur der Teilungsprodukte des Urans, welche von uns durchgeführt wurde.

Zur Herstellung der Umwandlungsprodukten des Urans bedienten wir uns einer durch Paraffin verlangsamter Neutronenstrahlung, welche mit dem Zyklotron nach der Reaktion

$$ {}^{2}_{1}D + {}^{2}_{1}D \rightarrow {}^{3}_{2}He + {}^{1}_{0}n $$

erzeugt wurde. Die Intensität der Neutronenstrahlung betrug circa 20 Curie Rn+Be. Die entstehenden Teilungsprodukte des Urans wurden nach der Rückstossmethode auf einer Glassplatte, mit der die Oberfläche des bestrahlten U_3O_8 in einer Entfernung von 3 mm überdeckt worden war, gesammelt. Die auf diese Weise gesammelten Uranbruchstücke wurden von der Glassplatte gewöhnlich mit verdünnter Salzsäure (1 : 5) aufgelöst; in seltenen Fällen wurde statt Salzsäure, Schwefel- oder Salpetersäure verwandt. Zu der Lösung setzt man Metallsälze aller fünf analytischen Gruppen zu und ein oder mehrere Metalle werden alsdann durch geeignete chemische Operationen von allen übrigen abgetrennt und in Form einer schwerlöslichen Verbindung zur Messung gebracht. Die Messung geschah mittels eines Geiger-Müllerschen Zähler aus Duraluminium mit einer Wandstärke von 0.12 mm. Alle zur Messung gebrachten Niederschläge wurden vorher auf dem Filter getrocknet, in Zellophan eingewickelt und um den Zähler umgewandt.

Von den solange erforschten Teilungsprodukten des Urankernes sind die Isotope des Bariums und des Lanthans von chemischen Standpunkte aus am eingehensten, wir möchten sogar sagen, erschöpfend untersucht worden. Sehr einleuchtend wird das Auftreten von Caesium-, Rubidium- und der Edelgas-Isotopen bewiesen. Das Vorkommen der anderen Radioelemente unter den Umwandlungsprodukten des Urans wird dagegen bestritten; das gilt vor allem für Strontium, Tellur und die Halogenen.

Das Strontium wurde unter den Umwandlungsprodukten des Urans zuerst von O. Hahn u. F. Strassmann ([10]) in überzeugender Weise nachgewiesen. Doch konnten die holländischen Forscher in einer darauffolgenden Arbeit ([8]) diese Auffindung von O. Hahn und F. Strassmann nicht bestätigen, was das ganze Teilungsschema (3) unter die Frage stellt. Es schien uns darum von Interesse die Anwesenheit von Radiostrontium unter den Teilungsprodukten des Urans nachzuprüfen. Zu diesem Zwecke wurden die auf der Glassplatte angesammelten Teilungsprodukte in verdünnter Salzsäure gelöst, zu der Lösung 0.02—0.03 g $KHSbO_4$, 0.02—0.03 g $La(NO_3)_3$ aq., 0.2 g $BaCl_2 \cdot 2H_2O$ und 0.3 g $SrCl_2 \cdot 6H_2O$ zugesetzt, und alsdann das Antimon mittels Schwefelwasserstoff aus salzsaurer Lösung als Sulfid, aus dem Filtrat Lanthan als $La(OH)_3$ mit Ammoniak und schliesslich das Strontium zusammen mit Barium mit kohlensaurem Ammonium gefällt. Die so erhaltenen Karbonate des Strontiums und Bariums wurden gut ausgewaschen und in Salzsäure aufgelöst. Die Lösung wurde mit Natriumacetat zur Abstumpfung der Salzsäure versetzt und das Bariums von dem Strontium als Chromat getrennt. Das Bariumchromat wurde nach dem Auswaschen und Trocknen auf seine Aktivität geprüft. Aus dem Filtrat wurde nach der Bariumfällung Strontium als Sulfat mit verdünnter Schwefelsäure und Alkohol

niedergeschlagen, abfiltriert, ausgewaschen, getrocknet und zur Messung gebracht. Beide Niederschläge erwiesen sich als aktiv. Beim Strontiumsulfat fanden wir stets zwei Aktivitäten, die eine mit $T \sim 7^h 30^m$ und die zweite mit einer viel grösseren Halbwertszeit, die solange noch nicht näher bestimmt wurde.

Die Halogene. Von den Halogenen wurden unter den Umwandlungsprodukten des Urans Brom ([4]) und Jod ([5], [6], [9]) gefunden. Doch sind die von den obenerwähnten Autoren verwandte Trennungsmethoden der Halogene, soweit man nach dem veröffentlichten Material beurteilen kann, nicht spezifisch genug (die Destillation einer Schwefelsäurenlösung unter Zusatz von Kaliumpermanganat oder Fällung mit Silbernitrat aus Salpetersäurenlösung). Von ganz besonderem Interesse wäre es dabei die Anwesenheit von Radiojod zu beweisen, da gerade Jod von verschiedenen Autoren als Teilungsprodukt beschrieben wurde, und zwar mit einer Halbwertszeit $T \sim \sim 2^h\ 30^m$, die mit T von Ekaplatin, welches aus Ekairidium mit $T = = 66^h$ entsteht, übereinstimmt. Um das Radiojod zu bestimmen, verfuhren wir wie folgt.

Das mit langsamen Neutronen bestrahlte Natriumpyrouranat wurde in verdünnter Schwefelsäure (1 : 5) gelöst, zu der Lösung etwas Kaliumjodid und Kaliumbromid zugesetz, die Lösung in das Destillationsapparat gebracht und nach Zusatz von etwas Natriumnitrit das Jod in eine Vorlage, die etwas Kaliumjodid und Wasser enthielt, überdestilliert. Nach dem Abschluss der Destillation wurde das Jod in der Vorlage als AgJ mit Silbernitrat niedergeschlagen. Das ausgeschiedene Silberjodid wurde abfiltriert, ausgewaschen, auf dem Filter getrocknet und zur Messung gebracht. Die Aktivitätsabfallkurve wies auf die Gegenwart zweier Isotope von Jod mit $T \sim 3.8^h$ und $T \sim \sim 28^h$ an. Dieselben zwei Jodisotope lassen sich auch unmittelbar aus den Uranbruchstücken, die nach der Rückstossmethode auf einer Glassplatte gesammelt wurden, isolieren. Ausser der Destillationsmethode wurde zur Jodisolierung auch die Extraktion des mit Natriumnitrit in Schwefelsäure ausgeschiedenen Jods mittels Chloroform oder Tetrachlorkohlenstoff verwandt. Das nach der letzten Methode abgetrennte Jod wies dieselben zwei radioaktiven Isotope auf. Die von uns aufgefundenen Jodisotope mit $T \sim 3.8^h$ und $T \sim 28^h$ stimmen nicht gut mit den von anderen Autoren angegebenen $T \sim 2.5^h$ und $T \sim 22^h$ überein. Von besonderem Interesse ist es, dass es uns nicht gelungen ist das Radiojod mit $T \sim 2.5^h$ unter den Umwandlungsprodukten des Urans aufzufinden. Ob ausser diesen zwei Jodisotopen noch andere mit erheblich kleinerer Halbwertszeit oder mit erheblich grösserer Halbwertszeit existieren, werden wohl nachfolgende Experimente entscheiden.

Ausser Jod gelang es uns unter den Teilungsprodukten des Urans auch Brom mit Sicherheit nachzuweisen. Um Bromabtrennung zu erzielen wurde wie folgt verfahren: zu der Lösung, die etwas Kaliumbromid enthielt, wurde, nachdem das Jod überdestilliert worden war, ein wenig Kaliumbichromat zugegeben, und die Destillation weiter fortgesetzt. Das nun jetzt übergehende Brom wurde in eine zweite Vorlage, die etwas Na_2SO_3 oder KJ-Lösung enthielt, aufgefangen. Das Brom allein oder in zweitem Falle zusammen mit Jod wurde nachher mit Silbernitrat niedergeschlagen, abfiltriert, ausgewaschen, getrocknet und die Aktivität des Niederschlages gemessen. In allen Fällen erwies sich das überdestillierte Brom als aktiv: die Zerfallskurve liess zwei Bromisotope erkennen, und zwar mit $T \sim 90^m$ und $T \sim 15^h$.

Zum Schluss sei noch erwähnt, dass falls die Jod-Brom Trennung nicht genügend scharf durchgeführt wird, so findet man leicht statt Jod mit $T \sim 3.8^h$ das Jod mit $T \sim 2.5^h$, und statt Jod mit $T \sim 28^h$ das Jodisotop mit $T \sim 22^h$. Die Aktivitätsabfallkurven für Jod und Brom sind auf den Abb. 1 und 2 wiedergegeben.

Das obenerwähnte erlaubt uns folgendes über die chemische Natur der Teilungsprodukte des Urans zu behaupten.

1. Unter den Teilungsprodukten des Urans treten Isotope von Strontium auf und zwar sind solange zwei Strontiumisotope, das eine mit $T \sim 7^h$ 30^m und das zweite mit einer viel grösseren Halbwertszeit, aufgefunden. Ausserdem finden sich unter den Teilungsprodukten auch Halogene

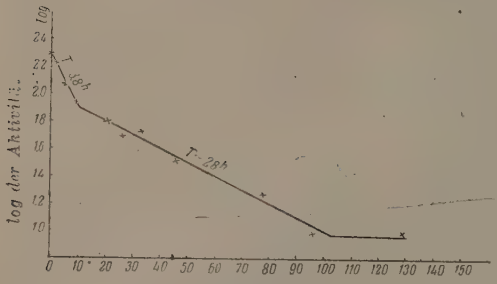

Abb. 1.

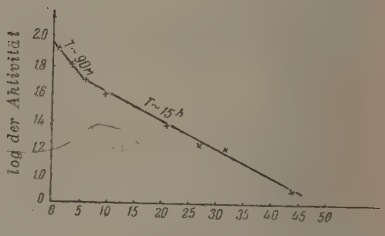

Abb. 2.

und zwar zwei Jodisotope mit $T \sim 3.8^h$ und $T \sim 28^h$ und vielleicht noch ein drittes mit bedeutend grösserer Lebensdauer, und zwei Bromisotope mit $T \sim 90^m$ und $T \sim 15^h$.

2. Die Anwesenheit von Jod und Brom unter den Umwandlungsprodukten des Urans weist darauf hin, dass auch andere Teilungsschemata ausser den von F. Joliot, J. Meitner u. O. Frisch und O. Hahn u. F. Strassmann vorgeschlagenen wohl möglich sind.

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PHYSIK

ZUR FRAGE ÜBER DIE CHEMISCHE NATUR DER PRODUKTE, WELCHE BEI DER TEILUNG DES URANKERNES UNTER EINWIRKUNG VON NEUTRONEN ENTSTEHEN. II

Von V. G. CHLOPIN, Mitglied der Akademie, M. A. PASWIK-CHLOPIN und N. F. VOLKOV

In der vorhergehenden Mitteilung gelang es uns zu zeigen, dass die unter der Einwirkung der Neutronen entstehenden Teilungsprodukte des Urans, ausser den schon früher beschriebenen Elementen, auch noch die Halogene, Radiojod und Radiobrom enthalten. Das Vorhandensein der Halogene veranlasste uns zu behaupten, dass ausser den drei von F. Joliot [3], O. Hahn u. F. Strassmann [1] und L. Meitner u. O. Frisch [2] aufgestellten Teilungsschemata des Urans auch noch andere existieren. Die Entdeckung der Halogene unter den Teilungsprodukten des Urans lässt das Auftreten unter diesen Teilungsprodukten der links von den Halogenen in der Periodischen Tafel stehenden Elemente, d. h. Tellur, Antimon, Zinn einerseits, und Selen, Arsenic und Germanium andererseits, erwarten. In der vorliegenden Mitteilung werden wir einige Versuche beschreiben, die uns anzunehmen zwingen, dass unter den Teilungsprodukten des Urans auch Antimon und Tellur auftreten.

Erst nach dem Abschlusse dieser Arbeit sind uns die Arbeiten von Ph. Abelson [4,5] bekannt geworden, in denen er mehrere Isotope von Antimon und Tellur unter den Teilungsprodukten des Urans beschreibt. Leider werden jedoch die von dem Autor in diesen Arbeiten zur Trennung verschiedener Elemente verwandten chemischen Methoden nicht eingehend genug beschrieben und scheinen deshalb zu einwandfreier Trennung dieser Elemente nicht ganz geeignet. Solange sind vier Isotope des Antimons mit $T \sim 5^m$; $T < 15^m$; $T \sim 40^m$ und $T \sim 4.6^h$ und sieben Isotope des Tellurs mit $T \sim 25^m$; $T \sim 30^m$; $T \sim 40^m$; $T \sim 70^m$; $T \sim 10^h$; $T \sim 30^h$ und $T \sim 72^h$ unter den Umwandlungsprodukten des Urans von verschiedenen Autoren und vor allem von Abelson [4,5] beschrieben worden.

In erster Linie stellten wir uns die Aufgabe die Anwesenheit von Antimonisotope unter Teilungsprodukten des Urans zu prüfen. Zu diesem Zwecke wurden die Antimonisotope nach zwei verschiedenen Methoden von den übrigen Elementen getrennt. Nach der ersten Methode wurde zu einer salz- oder salpetersauren Lösung, die Umwandlungsprodukte des Urans enthielt, ein wenig Antimon- und Bismutsalz zugesetzt, das Antimon samt Bismut durch Hydrolyse als meta-Antimonsäure niedergeschlagen, abfiltriert, ausgewaschen und die beiden Elemente durch Behandeln mit warmem gelben Schwefelammonium getrennt. Die Antimon als Sulfosalz enthaltende Lösung wurde von Bismutsulfid getrennt, und aus der Lösung nach dem Ansäuren mittels verdünnter Salzsäure das Antimonsulfid gefällt, abfiltriert,

ausgewaschen, getrocknet und zur Messung gebracht. Nach der zweiten Methode, wurde das bestrahlte Natriumpyrouranat oder die mittels der Rückstossmethode auf einer Glassplatte gesammelten Teilungsprodukte des Urans in verdünnter Schwefelsäure (1 : 4) gelöst und nach Zusatz von Antimonsalz und metallischem Zink, das Antimon als SbH_3 überdestilliert und in eine Lösung von $AgNO_3$ aufgefangen. Das sich in der Vorlage abscheidende Ag_3Sb wurde abfiltriert, gewaschen, getrocknet und seine Aktivität bestimmt. In beiden Fällen erwiesen sich die Antimonenthaltende Niederschläge als aktiv, so dass man nach der Aktivitätsabfallkurve zwei Antimonisotope bestimmen konnte, den einen mit $T \sim 12^m$, und den anderen mit $T \sim 17^h$.

Aus dem Verlauf der Aktivitätskurve ist es zu ersehen, dass sie nach einem schnellen Abfall der Aktivität einen ziemlich schnell verlaufenden Anstieg der Aktivität aufweist, um nachher mit einer Halbwertszeit von circa 17^h abzuklingen. Der Gang der Abfallskurve weist allem Anscheine nach auf die Anwesenheit von zwei Antimonisotopen mit $T \sim 12^m$ und $T \sim 17^h$, aus dem ein Tellurisotop mit $T \sim 40^m$ entsteht.

Der Versuch eine den experimentell gefundenen Werten entsprechende theoretische Kurve aufzubauen schlug aber fehl. Das veranlasste uns anzunehmen, dass die von uns abgetrennten Antimonisotope nicht genügend rein waren und wahrscheinlich noch andere radioaktive von uns noch nicht näher untersuchte Elemente enthielten. Dieser Umstand wird wahrscheinlich eine Änderung der Halbwertszeit, welche wir vorläufig den Antimonisotopen zuschreiben, hervorrufen.

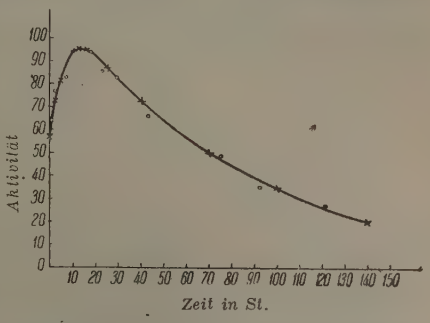
Um die Anwesenheit des Tellurs unter den Umwandlungsprodukten des Urans nachzuweisen und zugleich nachzuprüfen, ob das früher von O. Hahn und L. Meitner [6] entdeckte Ekairidium mit dem Radiotellur identisch ist, wie es von Ph. Abelson [7] und Bretscher a. Cook [8] behauptet wurde, haben wir auf folgende Weise verfahren.

Natriumpyrouranat wurde durch verlangsamte auf dem Zyclotron erzeugte Neutronen während 36 Stunden bestrahlt, in Salzsäure gelöst und die Lösung solange mit Salzsäure versetzt, bis die Säurestärke 7—8% betrug; alsdann wurde zu der Lösung 0.02—0.03 g K_2PtCl_4, 0.02—0.03 g $La(NO_3)_3$ aq. zugegeben und das Platin aus einer fast bis zum Kochen erwärmten Lösung mittels Schwefelwasserstoff als Platinsulfid gefällt. Der Niederschlag wurde abfiltriert, ausgewaschen und samt dem Filter in einen zur Herstellung des Natriumtellurid nach der Methode von L. Tschugaeff und V. Chlopin [9] dienenden Apparat untergebracht, mit 40 cm^3 10% NaOH, 0.1 g metallisches Tellurs und 0.4 g Natriumhydrosulfit versetzt, und das Gemisch auf einem Wasserbade unter Durchleiten von Wasserstoff eine halbe Stunde unter Umrühren erwärmt. Nachdem das zugesetzte Tellur unter Bildung von Natriumtellurid in Lösung überging, wurde es im Wasserstoffstrom von PtS und $La(OH)_3$ filtriert und das Tellur aus der Lösung durch Erwärmen auf dem Wasserbade unter gleichzeitigem Durchleiten von Luft als Metall wiedergefällt. Es scheidet sich unter diesen Bedingungen in glänzenden Blättchen aus, wird abfiltriert, mit Wasser ausgewaschen, getrocknet und zur Messung gebracht.

Alle Messungen wurden mit Hilfe eines Geiger-Müllerschen Zählers aus Duraluminium, mit 0.12 mm Wandstärke, ausgeführt. Die nach der obenerwähnten Methode erhaltenen Tellurniederschläge erwiesen sich aktiv, und die Abhängigkeit der Aktivität von der Zeit liess sich stets durch die auf Abb. 1 wiedergegebene Abfallskurve ausdrücken (Abb. 1). Wie aus dem Diagramm zu ersehen ist, weist die Aktivitätskurve zunächst einen gut ausgeprägten Anstieg, erreicht nach circa 14^h ein Maximum und fällt alsdann mit einer Halbwertszeit von 56^h ab. Die Analyse dieser Aktivitäts-

kurve liess die Bildung aus dem Tellur mit $T\sim 56^h$ eines Jodisotopen mit $T\sim 3.8^h$ feststellen, was mit den in unserer ersten Mitteilung über Radiojod angeführten Angaben durchaus übereinstimmt.

Auf der Abb. 1 sind durch Kreise die experimentell gefundenen Werte angegeben, die theoretisch, und zwar unter der Annahme, dass dem Tellur eine Halbwertszeit von 56^h und dem Jod—3.8^h zukommt, berechneten Werte sind durch Kreuze bezeichnet. Wie es zu ersehen ist, stimmen die experimentell gefundenen Werte mit der theoretischen Kurve innerhalb Versuchsfehler überein. Diese Tatsache kann als weiterer Beweis für der Reinheit des abgetrennten Tellurs dienen. Die von uns für die Tellurtrennung verwandte Methode erlaubt dessen vollkommene Trennung von allen schweren Metallen, die unlösliche Sulfide und Hydroxyde bilden, oder verhältnismässig leicht zu elementarem Zustande reduziert werden können. Doch ist die Anwesenheit von kleinen Mengen Selen in dem abgeschiedenen Tellur nicht ausgeschlossen, da Selen unter Einwirkung der alkalischen Hydrosulfitlösung, obwohl viel schwerer, auch Natriumselenid zu bilden vermag. Weitere Versuche sollen zeigen, ob auch Selen unter den Teilungsprodukten des Urans auftritt, und wenn dies der Fall ist, in wieweit dessen Anwesenheit die von uns angegebene Halbwertszeit des Tellurs beeinträchtigen mag.



Zum Schluss sei noch erwähnt, dass Platinsulfid Niederschlag, falls er aus einer Uranlösung, die vorher längere Zeit (2 Monate) mit langsamen Neutronen von einer konstanten Neutronenquelle (RdTh+Be) bestrahlt wurde, erzeugt wird, nach dem Zerfall des Elementes mit $T\sim 66—70^h$ noch eine Restaktivität aufweist, welche mit einer Halbwertszeit circa 60 Tage zerfällt. Eine ähnliche Restaktivität weisen auch Antimonniederschläge auf. Da ein Radioantimon mit $T\sim 60$ Tage bekannt ist, so halten wir es für wahrscheinlich, dass die von uns beobachtete Restaktivität einem Antimonisotop mit $T\sim 60$ Tage zuzuschreiben ist. Die Restaktivität des Platinsulfidniederschlags mit dergleichen Halbwertszeit wurde von O. Hahn, L. Meitner und F. Strassmann im Jahre 1938 beobachtet und einem isomeren Ekairidium zugeschrieben ([10]).

Schliesslich sei noch betont, dass die Antimonniederschläge ausser einem Radioelement mit $T\sim 60$ Tage noch eine Restaktivität, der man eine Halbwertszeit von 112—115 Tage zuzuschreiben muss, aufweisen. Diese Restaktivität ist von uns noch nicht näher untersucht worden.

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PHYSICS

AN ATTEMPT TO DETECT THE FORMATION AND FISSION OF TRANSURANIUM NUCLEI

By A. E. POLESSITSKY and K. A. PETRJAK

(Communicated by V. G. Chlopin, Member of the Academy, 31. VII. 1939)

Experiments by Green and Alvarez (1) and Feather (2) showed uranium fission under neutron bombardment to go on very quickly. However, simultaneous formation of transuranium elements, most probably of β-radioactive ones, is also possible (3). The products of β-decay may be excited nuclei which also undergo fission immediately after their formation.

This process may possibly account for the delayed neutron emission from irradiated uranium (4) as well as for the activation of the paper placed on irradiated uranium observed by Volkov (5). The effective cross-section of formation of transuranium elements must, at any rate, be smaller than that of uranium fission. Moreover, the intensity of their fission must be limited by the rate of their formation through β-decay. Thus, the intensity of the fission of transuranium elements after irradiation must be much smaller than that of uranium in the course of irradiation, and it might therefore have been overlooked by Green and Alvarez.

For a more sensitive proof of such a process we bombarded 50 g of U by slow neutrons from the cyclotron of the Radium Institute. The intensity of the neutron beam passing through U was equivalent to 5—10 g Ra+Be. After a 20-hour bombardment the uranium salt was dissolved in HCl and a few mgs of PtS_2 were precipitated in the usual way, together with all the transuranium elements in case such were formed. The precipitate measured on a Geiger-Müller counter gave several hundreds of impulses per minute (correction being made for the activity of the UX adsorbed). The same precipitate placed in an ionization chamber of the Wynn-Williams type gave no effect within two hours. The investigation of such a precipitate in a Wilson chamber, kindly made by N. A. Perfilov to whom thanks are due, also gave a negative result.

This experiment shows that if transuranium elements are formed from uranium bombarded with neutrons, after which they undergo fission, the effective cross-section for this process must be much smaller than that of uranium fission, and at any rate no greater than 10^{-28} cm².

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PHYSICS

ELECTRICAL RESISTANCE OF SINGLE CRYSTALS OF ZINC AND CADMIUM IN A MAGNETIC FIELD AT LOW TEMPERATURES

By B. G. LAZAREV, N. M. NAKHIMOVICH and E. A. PARFENOVA

(Communicated by S. I. Wawilow, Member of the Academy, 25. VII. 1939)

1. The increase in the resistance of metallic single crystals in a transverse field depends on the angles made by the current and the field with the axes of the crystalline lattice, and this «orientation effect» increases with decreas ng temperatures. The investigations of Justi and Scheffers (1) have revealed the existence of such anisotropy in many metals of cubic system showing isotropic conduction in the absence of the magnetic field. For uncubic metals, of which gallium and bismuth (2) have been studied in detail by De-Haas and others, the anisotropy of the resistance in the magnetic field is still more pronounced. These effects testify to the need for the theory to take account of the interaction between the electrons and the crystalline lattice.

In the present work the behaviour of the resistance of single crystals of hexagonal zinc and cadmium in magnetic fields up to 18 kilogauss is examined from the viewpoint of how this interaction is influenced by the crystal structure. A substantial dependence of the effect on the orientation of the crystal axes was observed both for zinc (3) and for cadmium (4) at liquid-nitrogen temperature. The increase of the resistance in a longitudinal magnetic field was investigated less extensively than the transverse effect. This effect for Zn and Cd is also being studied in this work.

2. Most of the single crystals were obtained from Hilger Zn and Cd («for spectroscopy»), partly by Bridgman's method (5), partly by the method of Kapitza (6). The small residual resistance of the specimens shows the insignificance of the impurities. Angle α between the basal plane and the axis of the specimen and angle β between the axis [1000] lying in the basal plane and the specimen axis were determined with a goniometer by the method of Jakovleva (7). For most investigated single crystals $\alpha=\beta$, and only for Zn10 and Cd4 $\beta>\alpha$. A compensation scheme permitted to measure the resistance to $10^{-7}\Omega$.

3. When a single crystal with the basal plane nearly parallel to the specimen axis is rotated in a transverse magnetic field at $T\sim80°$ K, the rotation diagram is periodical curve with a maximum where the basal plane is at right angles to the field, and a minimum where they are parallel. At $T=4.2°$K the magnitude of the effect for the single crystal of the same orientation increases and the diagram becomes more complicated (Fig. 1). The maximum at $\Theta=90°$ is replaced by a minimum less deep than that at $\Theta=0°$, and additional bends appear at $\Theta=\pm30°$. As the temperature is raised and the field diminishes, the maxima and minima of the diagram smooth out. Fig. 2 represents the rotation diagram at 4.2° K of a single Cd crystal with the same basal plane orientation. It is almost identical with the diagram for zinc.

The variation of the dependence of the field on the increase in resistance at characteristic angles of the rotation diagram is of interest. In Fig. 3 are

given such curves corresponding to $\Theta=0^\circ$ and $\Theta=90^\circ$ of Fig. 1. Not only do they differ in character, but at $\Theta=90^\circ$ the dependence is a function with a non-monotonous derivative. As seen from Fig. 3, this anomalous depen-

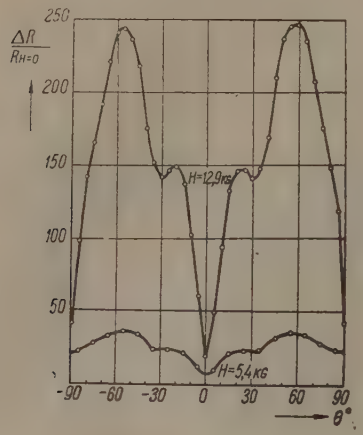
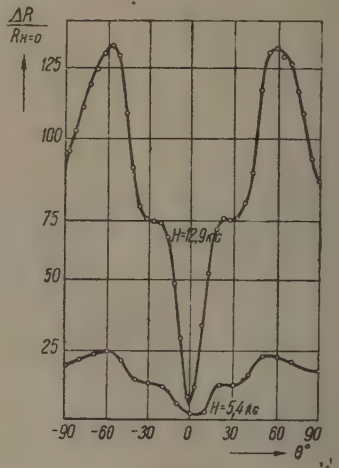


Fig. 1.



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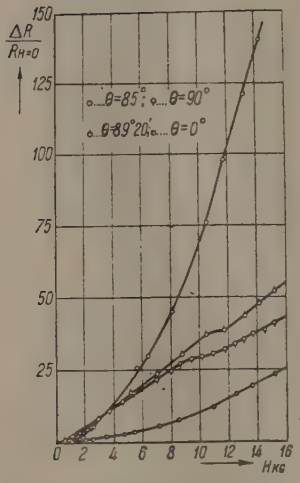

Fig. 3.

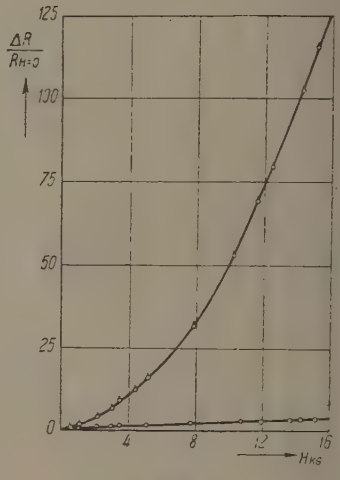

Fig. 4.

dence is confined to a narrow angle interval and is completely smoothed out at $\Theta=85^\circ$. On taking single crystals with a successively increasing angle α the character of the rotation diagram will gradually change, so that at $\alpha\approx90^\circ$ the curve will have 3 maxima if the specimen is rotated through 180°, rotation being about a hexagonal axis.

In Table 1 are given for the zinc specimen the ratio $R_T/R_{0^\circ C}$, the anisotropy of the rotation diagram $\left(\frac{\Delta R_{max}}{\Delta R_{min}}\right)$, and the transverse effect averaged over the angles of the diagram at $T=20.4$ and 4.2° K. It is seen that for Zn the mean transverse effect at $H=$const diminishes as α increases.

Table 1

	α, angle between the basal plane and the wire length	$\frac{R_{20.4^\circ}}{R_{0^\circ C}} \times 10^4$	$\frac{R_{4.2^\circ}}{R_{0^\circ C}} \times 10^4$	$T=20.4^\circ K, H=11.5$ kG		$T=4.2^\circ K, H=12.9$ kG	
				$\frac{\Delta R_{max}}{\Delta R_{min}}$	$\frac{\overline{\Delta R}_\perp}{R_{0^\circ C}} \times 10^4$	$\frac{\Delta R_{max}}{\Delta R_{min}}$	$\frac{\overline{\Delta R}_\perp}{R_{0^\circ C}} \times 10^3$
Zn4	2°	58	$4_{.0}$	1.5_2	12_2	—	—
Zn10	2°	57	$4_{.7}$	1.5_8	12_4	14.4	75
Zn2	4°	62	—	1.5_2	11_6	—	—
Zn8	5°	—	$5_{.6}$	—	—	8.2	62
Zn12	10°	62	—	—	—	9.7	80
Zn7	19°	68	$5_{.8}$	1.4_5	11_5	4.2	41
Zn15	24°	60	$3_{.7}$	1.2_{16}	11_3	2.3	64
Zn5	41°	65	$6_{.2}$	—	—	2.9	52
Zn6	75°	87	$3_{.6}$	1.1_0	9_1	1.6	69
Zn17	80°	—	$7_{.6}$	—	—	1.2	48
Zn14	85°	172	$4_{.9}$	—	5_2	1.1	35
Zn1	Polycr.	67	—	—	10_7	—	—
Zn9	Polycr.	59	$5_{.7}$	—	10_6	—	55

At helium temperature it is moreover largely affected by the residual resistance of the specimen. The data for Cd also confirm this dependence on α. The effect for polycrystals is approximately an average of the single crystals of limit orientations.

4. Fig. 4 represents the dependence of the resistance increase on the field in transverse and longitudinal field for a polycrystal of zinc at 4.2° K. The longitudinal effect markedly differs from the transverse one by its character of saturation. The longitudinal and transverse effects for polycrystalline Cd have the same character as established by Milner ([8]). At liquid-hydrogen temperature the longitudinal effect also has the character of saturation. At liquid-nitrogen temperature a dependence without saturation symptom was established for the longitudinal effect in both metals ([3],[9]).

5. The identity of the saturation phenomena in the longitudinal effect of Zn and Cd at 20.4 and 4.2° K seems to be due to the similarity of their structure. We studied the dependence of the longitudinal effect on the electron-lattice interaction by measuring the longitudinal effect in single crystals with differently oriented basal planes. It was found, as shown in Table 2, that the longitudinal effect at $T=20.4^\circ$ K has a maximum in the vicinity of $\alpha=45^\circ$. Secondly, it was found that at hydrogen temperature as well as at nitrogen and room temperatures ([3]) when the specimen is rotated about an axis perpendicular to the current and the field and parallel to the basal plane, the maximum and minimum of the diagram coincide respectively with the longitudinal and transverse position of the specimen only at $\alpha \sim 0^\circ$ and $\alpha \sim 90^\circ$. At intermediate orientations the minimum is shifted towards the place where the basal plane approaches to an orientation parallel with regard to the field. At helium temperature these two phenomena are almost imperceptible, probably owing to the increased influence of even small departures from the parallelism of the current to the field.

6. The Franck-Sommerfeld theory ([10]) fails to give a correct description of the transverse effect, because it disregards the anisotropy of the electron bonds in the lattice. However, by taking formally account of this anisotropy one arrives at the result that the effect must increase with increasing fluctuations of the time intervals between collisions. It may be assumed that

Table 2

	α, angle between the basal plane and the wire length	$T = 20.4°K$, $H = 11.5$ kG	$T = 42°K$, $H = 11.5$ kG	
		$\frac{\Delta R_{\parallel}}{R_{0°C}} \times 10^4$	$\frac{\Delta R_{\parallel}}{R_{0°C}} \times 10^4$	$\frac{R}{R_{0°C}} \times 10^4$
Zn4	2°	3_5	6	10
Zn10	2°	3_4	3	12
Zn12	10°	4_3	—	—
Zn7	19°	6_1	26	32
Zn15	24°	5_5	17	21
Zn5	41°	8_0	—	—
Zn6	75°	4_6	33	37
Zn13	80°	2_3	—	—
Zn14	85°	1_4	—	—
Zn1	Polycr.	5_3	—	—
Zn9	Polycr.	4_7	16	21

in the case of a hexagonal lattice the fluctuations are the least when the current flows along the hexagonal axis. This may account for the dependence of the mean transverse effect on the orientation of the basal plane. The anomalous field dependence observed within a very narrow angle interval seems also to be due to the interaction of the electrons with the lattice.

The connexion of the rotation diagram with the crystal structure can be explained from the standpoint of the hypothesis of the current flowing preferentially along certain planes of a crystalline lattice. The basal plane along which the conduction is the highest must be such a plane. When the current is parallel to the basal plane and this is parallel to the field, the Lorentz force tends to divert the electrons from the basal plane. But owing to the large directing action in this plane the resulting deviation of the electron is less than, say, in the case of a Lorentz force parallel to the basal plane. This accounts for the minimum of the resistance increase at $\Theta = 0°$. The second maximum at $\Theta = 90°$ which occurs at a lower temperature can be attributed to an analogous effect of the lateral planes of the prism. The results on single crystals of other metals permit the same explanation.

7. The hypothesis of the «plane propagation» of the current affords an explanation for the dependence of the longitudinal effect on orientation and for the displacement of the minimum in the rotation diagram (§ 5), namely, that the «true» longitudinal effect at $\alpha = 0°$ and $\alpha = 90°$ is increased by a contribution from the microscopic components of current perpendicular to the field which are produced by the directing force acting on the electrons in the basal plane.

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PHYSICS

ON THE TRANSITION MAXIMUM ACCORDING TO THE DATA OF OBSERVATIONS FROM SUBSTRATOSTATS

By S. N. VERNOV

(Communicated by S. I. Wawilow, Member of the Academy, 25. VII. 1939)

Investigations of the latitude effect of cosmic rays in the stratosphere (1) show that electrons with an energy of several milliards of volts on passing through a substance with a small atomic number undergo an energy loss considerably greater than the energy loss by ionization. Comparison of experimental data on the latitude effect in the stratosphere with deductions from the cascade theory show good agreement between the two.

However, as was pointed out by Skobeltzyn (2) immediately after publication of the work on the cascade theory, a number of experimental facts relating to the transition effect (from air to lead) are in sharp contradiction with deductions from the cascade theory in the form in which it is applied in literature to interpret the effects caused by cosmic rays (3).

According to the cascade theory, when electrons and photons enter lead from the air, there should be observed a considerable increase in the number of particles on account of cascade processes in the lead. However, experiments by Frank-Kamenetsky (Diploma thesis) and Schindler (4) and Street and Young (5) show that the number of ionized particles is hardly increased at all. Examination of curves of the transition effect makes it possible to establish the following divergences between the cascade theory (without scattering being taken into account) and experimental data.

1) The increase in the number of particles (threefold) which is required by the theory, after cosmic rays have passed through 1.5 cm of Pb, is not observed experimentally.

2) A considerable fraction of the particles of the soft component have too great a penetrating power (there is a «tail» in the absorption curve of the soft component for large thicknesses of lead).

3) If scattering is not taken into account, the total energy which is absorbed in the lead is three times that required for ionization. Indeed, comparison of absorption curves for different materials shows (4) that the area under the absorption curve (in Al) of the soft component is about three times as great as the area under the respective curve (for Pb), if the scale along the axis of abscissae is so chosen that the energy losses by ionization are identical (6). Since the area under the curve gives the total quantity of energy which is absorbed, the reduction in this area (for Pb) shows that the effective energy losses in lead are considerably greater than the ionization losses (without scattering being taken into account).

However, it should be noticed that the above-mentioned [8] contradictions with the cascade theory of Bhabha-Heitler [7]-Arley [8] will only occur, if at sea level and low altitudes the soft component consists entirely of electrons and photons. However, the probability does not seem excluded that in addition to mesotrons of great energy, and consequently of great penetrating power, there are also secondary mesotrons with little energy. Proceeding from the assumption of the presence of low energy mesotrons, the contradictions involved in the value of the maximum and the «tail» in the absorption curve of the soft component may be avoided. Indeed, if electrons constitute but a small fraction of the soft component, the «tail» in the absorption curve may be entirely put down to the account of secondary mesotrons. The curve for electrons might then show an appreciable maximum. It should be noticed that explanation of the third contradiction meets with certain difficulties connected with the circumstance that it would be necessary to attribute to slow mesotrons an absorption varying with material.

At an altitude of 8—10 km the intensity of the penetrating component forms less than a fifth of the total intensity of cosmic rays. At the same time, at this altitude there should also be electrons present, produced as a result of cascade processes in the atmosphere at the expense of primary electrons with an energy of 10^9—10^{10} V, the presence of which has been established by latitude experiments in the stratosphere. Therefore at least 80% of all the particles at an altitude of 8—10 km should be electrons. Thus, measurements of the increase in the number of particles when a lead plate is placed over the instrument at an altitude of 8—10 km makes it possible to determine the form of the absorption curve for electrons. In view of this we carried out such experiments during two substratostat flights.

In order to measure the intensity of cosmic radiation we used our instrument with one Geiger-Müller counter. On account of the small size of the counter (7 mm diam., length 12 mm) it was possible to situate the lead plate at a not very great distance from the counter and thus create conditions under which a simultaneous entry of two particles into the counter was scarcely probable. In our experiments the lead plate was situated over the instrument at such a distance that if the particles emerging from the lead diverged by more than 4 — 5°, they could not possibly enter the counter together. Even short path particles could enter the counter. Travelling from the lead to the inner volume of the counter, the particles had to pass through the following thicknesses: in the first flight 1.2 g/cm² and in the second 0.6 g/cm².

In the course of the flights the lead plate was shifted 36 cm every five minutes. In one of these positions it was situated over the counter. The lead plate used in the first flight was of the following dimensions: thickness 1.5 cm, area 30×30 cm². In the second flight, thickness 0.6 cm. Registration of the number of discharges in the counter during the flights was carried out with a mechanical counter, whose readings were recorded by the pilot P. P. Polosukhin every five minutes at the instant of shifting the lead plate. Records were taken simultaneously on a self-recording apparatus which we designed. In addition to this, radiosignals were transmitted in the same way as during flights of pilot-balloons. Even though the transmission and reception of radiosignals during the substratostat flights was rendered exceedingly difficult by the simultaneous transmissions from radiostations on the substratostat and on the earth and also owing to atmospherics, nevertheless the reception (though discontinuous) of radiosignals was desirable as a check on the correct operation of the counter. The reception of radiosignals showed that the counter was working normally in both flights.

The data obtained from the treatment of the readings of the self-recorder

coincide well with the indications of the mechanical counter. Data showing the dependence of the number of discharges on the altitude also testify to the correct functioning of the counters during the flights. The increase in the number of the particles with altitude was approximately the same in both flights and coincides with data obtained during the flights of pilot-balloons at similar latitudes.

The data obtained during the two flights are given in Figs. 1 and 2. Just as in the case of pilot-balloon flights, in order to ensure radioreception radioactive ore was placed close to the instrument, as a result of which the number of charges at low altitudes was considerably increased. It will be seen

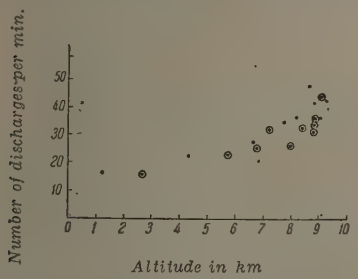

Fig. 1. First flight of substratostat, 4 Dec. 1938 (indications of mechanical counter); ● without Pb, ⊙ with 1.5 cm Pb.

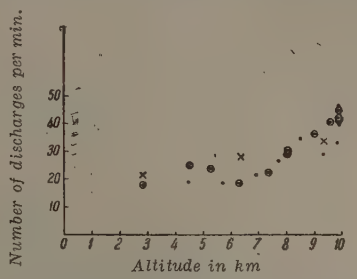

Fig. 2. Second flight of substratostat, 26 Feb. 1939 (indications of mechanical counter); without Pb: • up, × down; with 0.6 cm Pb: ⊙ up, ● down.

from Figs. 1 and 2 that, contrary to what should be expected from theory, no increase in the number of particles by several times was actually observed. Therefore the contradictions mentioned above are confirmed under conditions, in which it is possible to be certain that the radiation falling upon the lead consists mainly of electrons and photons.

On the basis of data obtained at altitudes of more than 8 km it may be established that when a lead plate of 1.5 cm is situated above the counter, a reduction in the number of cosmic particles of 20% is observed, whilst with a plate 0.6 cm thick there is an increase by 18%. These values are in acute contradiction with results calculated from the Bhabha-Heitler-Arley theory. Given the spectrum of the primary particles falling upon the top of the atmosphere, it is possible to determine the cascade curve in it. From these curves we found that at altitudes of 8—10 km the average energy per electron in the cascade is 2×10^8 V. Taking into account the geometrical conditions of our apparatus and the angular distribution of the cosmic rays at this altitude, it may be found from the cascade theory that when electrons with energies of 2×10^8 V fall upon a lead plate 0.6 cm thick, the number of particles should increase 3.5 times. With a lead plate 1.5 cm thick the number of particles should be 3 times greater than the initial number. Special calculations showed that the values for the increase in the number of particles are but very little altered by taking into account the presence of a considerable number of photons in the radiation falling upon the lead. In view of the fact that the height of the maximum in the cascade curves is approximately proportional to the energy of a primary electron, the energy distribution of the particles incident upon the plate is not essential for the calculations, since the sought for value is only determined by the mean electron energy.

There is thus considerable divergence between the experimental data obtained when the electrons passed through a substance with a high atomic number and those calculated from the theory of Bhabha-Heitler-Arley and Serber [9] (without taking scattering into account). It should be noticed that

if we proceed from the spectrum of particles in the cascade given by Arley, the effect of scattering cannot be great, since (according to Arley) only 15% of the particles in the cascade in lead have an energy of less than 3×10^6 V. The problem as to the causes of the divergence between theory and experiment noted above will be considered in the next article.

In conclusion the author considers it his duty to express his profound gratitude to S. I. Wawilow and to D. B. Skobeltzyn for valuable advices and help in carrying out the investigations. Thanks are also due to A. V. Mironov and S. E. Levit for their participation in the work, as well as to the pilots A. A. Fomin and P. P. Polosukhin for having carried out the measurements during the substratosphere flights.

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PHYSICS

ON CERTAIN DIVERGENCES BETWEEN EXPERIMENTAL DATA AND DEDUCTIONS FROM THE BHABHA-HEITLER-ARLEY CASCADE THEORY

By S. N. VERNOV

(Communicated by S. I. Wawilow, Member of the Academy, 25. VII. 1939)

In the previous article we have pointed out that if one proceeds from the form of the spectrum of particles in the cascade given by Arley, it is possible to neglect the influence of scattering when examining the transition effect. However, it is doubtful whether this spectrum is correct. Indeed, this spectrum was obtained on the assumption that for all values of the energy above the critical one there are no energy losses on ionization, and on the other hand, there are only ionization energy losses for energies of less than the critical value. It is natural that this assumption having been made, the number of particles in the spectrum which are of low energy is sure to be underestimated. One may be assured from simple consideration that the deviations from the spectrum form suggested by Arley should be great. The form of the spectrum may be evaluated by subsequent approximations; proceeding from the spectrum observed in the absence of ionization losses for particles of all energies (this spectrum is determined from data given in Bhabha-Heitler's work), we may calculate the number and spectra distribution of the photons. Further, from the photon spectrum found above it is possible to determine the electron spectrum taking into account ionization losses for electrons of all energies. We then calculate the new photon spectrum which is in equilibrium with the electron spectrum obtained above when evaluating the ionization losses. The following approximation for the spectrum is then found by proceeding from the corrected photon spectrum. The form of the spectrum may be determined by a number of these successive approximations. Fig. 1 shows the results of our calculations

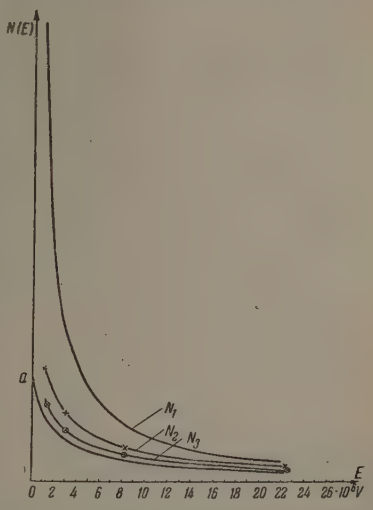

Fig. 1. Serber's cascade curve for $E_0 = 2 \cdot 10^8$ V.

(N_1 is the initial spectrum before ionization losses are made allowance for; N_2, the first approximation and N_3, the second one) where $N(E)$ is the number of electrons in the spectrum with energies greater than E. Curve a in Fig. 1 gives the spectrum obtained in the work by Tamm and Belenky ([1]). It will be seen that 60% of the particles in this spectrum have energies of less than 3×10^6 V, whilst in Arley's spectrum 15% of the particles showed energies of less than 3×10^6 V. Therefore the effect of scattering cannot be neglected, since, in opposition to Arley's spectrum, in the actual spectrum a considerable part of the particles have energies of a few million volts.

The incorrectness of Arley's spectrum and the presence of a large number of small energy electrons in the cascade may also be shown in a representative manner as follows. Let us examine Arley's spectrum for the case of equilibrium. In this spectrum the number of particles (within the given energy range) with energies of less than the critical value is constant. Above the critical value the number of particles falls as $1/E^2$. From formulae given in the work of Bhabha-Heitler it is possible to determine the photon spectrum which is in equilibrium with the given electron spectrum:

$$h(k)\,dk = b\frac{N(k)}{k}dk \qquad (1)$$

where $h(k)\,dk$ is the number of photons with energies between k and $k+dk$, $N(k)$ is the number of electrons with energies greater than k and b is a numerical coefficient. Knowing the number and spectral distribution of the photons, it is not difficult to determine the number of secondaries which will be formed by the photons in a thin layer of lead (say, 0.4 mm thick) and to find the number of these secondaries which come out of the layer. On the other hand, part of the electrons which fall upon the layer will be absorbed in it. If the examined spectrum is correct, the conditions of equilibrium should be fulfilled and the increase in the number of electrons at the expense of secondaries from the photons should be compensated by the absorption of low energy electrons. However, it may be shown that Arley's spectrum does not fulfill the conditions of equilibrium. The number of electrons with so low an energy (0.6×10^6 V) as to be absorbed in a 0.4 mm layer of lead is only 3% of the total number of particles in the cascade. However, the number of electrons which emerge from a 0.4 mm layer of lead at the expense of secondaries produced by the photons is about 50% of the total number of electrons in the cascade.

There is thus an acute internal contradiction in the Bhabha-Heitler-Arley theory, since the spectrum given by Arley for the case of equilibrium does not fulfill the conditions of equilibrium. It stands to reason that in an actual equilibrium spectrum there should be a considerably greater number of low energy electrons absorbed in a 0.4 mm layer of lead. Indeed, if analogous calculations are carried out on the basis of Tamm-Belenky's spectrum, the equilibrium conditions are fulfilled. The form of the spectrum may be evaluated by taking different values for the thickness of the layers. The results of our calculations are represented in Fig. 2. The solid line curve illustrates Tamm-Belenky's spectrum. There is satisfactory agreement within the low energy region.

The cascade theory implies the not altogether justifiable assumption of constancy of the cross-section for the Bremsestrahlung at all energies. Using the method examined above, it may be shown that if the dependence of the cross-section on the energy is taken into account [see Bhabha-Heitler ([2]) (Fig. 3)], the form of the spectrum of particles in the cascade is very little altered. Calculations show that the number of electrons with energies less than 3×10^6 V falls by only 1.2 times if the reduction in the cross-section

is taken into account for retardation at low energies. The Compton effect is also not taken into account by the cascade theory and is replaced by the «fictitious» process of formation at any energy, however small. However, this simplification can hardly have considerable influence on the form of the spectrum, since the spectral composition of Compton electrons and electrons (+and—) of pairs are close to each other. Special calculations showed that the average energy of particles in the Tamm-Belenky spectrum is in agreement with the cascade curves obtained by Serber.

In view of the fact that the spectrum of particles in a cascade in lead contains a considerable part of low energy particles, it is necessary to evaluate the influence of scattering. Owing to the presence of scattering, the secondary electrons which fall onto the instrument will be due to cosmic rays coming from some different angle to the vertical. Owing to the sharply pronounced

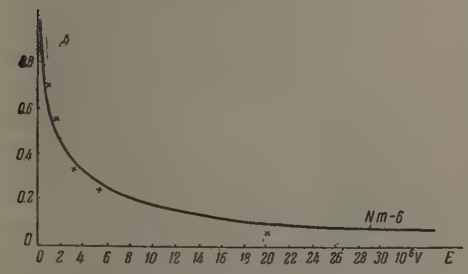

Fig. 2. Cascade curve after taking scattering into account.

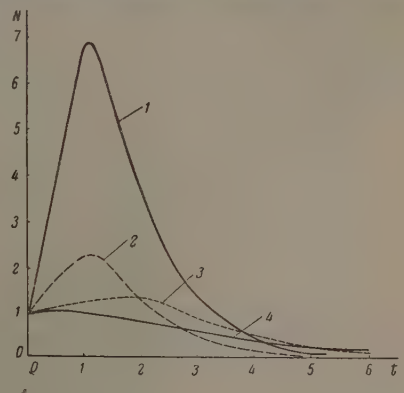

Fig. 3. Cascade curve after taking into account more penetrating γ-rays and scattering.

dependence of the intensity of cosmic radiation on the angle to the vertical, the intensity of the secondary radiation may be considerably reduced as a result of scattering. In order to evaluate the weakening of the secondary radiation, it is necessary to determine the angle of deviation of secondaries resulting from scattering.

The average projected angle in the case of multiple scattering is found from the formula:

$$\alpha_m = \frac{BS^{\frac{1}{2}}}{E} \qquad (2)$$

where S is the path of an electron and E its energy.

Electrons with an energy E are formed at the expense of electrons of greater energy. However, in view of the circumstance that scattering has an appreciable influence only on low energy electrons, the energy losses in this region are almost entirely reduced to ionization losses. Hence the energy of electrons may be expressed as a function of $S \cdot E = E' - \beta S$, where E' is the initial energy of an electron at the instant of its formation by a photon, and β, the energy loss per unit path. Taking into account that the mean square angle may be found by summation of the squares of the angles for the separate portions of the path, we have:

$$\alpha^2_{mean} = \int_0^S d\alpha^2_{mean} = \int_0^S \frac{B^2 dS}{E^2} = \int_0^S \frac{B^2 dS}{(E' - \beta S)^2} = \frac{B^2}{E^2} \frac{(E' - E)E}{\beta E'}.$$

The part played by electrons with a different energy E' in the formation of electrons E is determined from the form of the spectrum. It was found by calculation that for electrons with energies of 2×10^6, 4×10^6 and 6×10^6V half the particles are scattered through angles greater than 62, 43 and 35°, respectively.

In the case of low energy electrons the influence of scattering was also evaluated on the basis of the work by Bethe, Rose and Smith ([3]), since considerable errors might be obtained at large angles with the method of calculation described above.

The influence of scattering can be evaluated from this. Calculations show that the intensity of secondary radiation may be weakened some two or three times by scattering. Therefore the circumstance that the energy losses in lead are two or three times greater than the ionization losses, which is mentioned in our previous article, may be attributed to scattering. It should be mentioned that the influence of the walls of the instrument (1—2 mm of brass) was taken into account in making the calculations.

By taking the scattering into account, it is possible to remove the third of the contradictions mentioned in the previous article. The height of the maximum is simultaneously reduced some two or three times.

However, the second contradiction associated with the presence of a considerable «tail» in the experimental curve becomes still more acute, since with great thicknesses of lead the influence of scattering should appear at any rate no less than it does with small thicknesses (Fig. 3). Yet, it may be mentioned that there are simplifications made in the cascade theory which may be the cause of this discrepancy between theory and experiment. In the cascade theory it is supposed that the cross-section for the production of a pair is of constant value for all energies. As a matter of fact the cross-section falls considerably as the energy is reduced. True enough, in the low energy region the cross-section increases for the Compton effect. As was found above, from the viewpoint of the cascade theory the Compton effect is to a considerable degree analogous with the process of pair-formation. Therefore, if the sum of the cross-sections for the two processes remains constant, it is permissible to consider this simplification in the initial assumption of the cascade theory as a correct one. From data given in Fig. 6 of Bethe-Heitler's article it may be established that in substances with a low atomic number the sum of the cross-section remains approximately constant down to very small energies. However, the position is very different in the case of lead. With energies of several million volts the photons have an absorption coefficient approximately three times less than the coefficient attributed to them by the cascade theory. In connexion with the circumstance that the number of low energy photons should be great, the energy of the photon cascade which is in equilibrium with the electron cascade increases considerably. This should lead to a change in the shape of the cascade curve, namely, it should be lengthened. If we suppose for sake of simplicity that the new cascade curve is similar to the initial one and differs from it only in the ordinate and abscissa scales, it may be shown that the effect under consideration should lead to a lengthening of the abscissa scale and a shortening of the ordinate one by 1.7 times. Fig. 3 gives curves which show the necessary changes in the cascade curve when scattering and the more penetrating γ-rays are taken into account.

We may thus draw the conclusion that the discrepancy between the Bhabha-Heitler-Arley cascade theory and the experimental data which is pointed out in the previous article may be entirely removed, without departing from the physical foundation of the cascade theory, since in opposition to the Arley spectrum the actual spectrum of particles in the cascade

contains a large number of low energy electrons, so that it is necessary to take into account scattering and the presence of low energy photons (with a small absorption coefficient).

Proceeding from our viewpoint, it is possible to explain many other effects besides the three main contradictions:

1) Owing to the presence in the cascade of a large number of low energy particles, an explanation of the experiments of Geiger and Zeiller ([4]) may be given. Calculations show that the probability of the counter operating owing to electrons in cascades is altogether twice the same probability for photons, which is in good agreement with Geiger and Zeiller's experiments.

2) In view of the circumstance that scattering has least influence of all with small thicknesses of lead, the maximum of the Schindler transition curve is displaced in the direction of small thicknesses as compared with the maximum in Serber's cascade curves.

3) Consideration of elastic scattering makes it possible to explain the intense divergibility of particles in cascades.

4) If the presence of scattering in lead is taken into account, it may be understood why the equilibrium intensity of delta-radiation which accompanies the penetrating component is less in heavy elements than in light ones.

5) Measurements which we carried out with two Geiger-Müller counters showed that a considerable number of low energy electrons emerge from lead.

6) A number of arguments of Euler and Heisenberg in favour of the existence of burst-showers should be questioned, since owing to the presence of scattering the number of cascade-showers from delta-electrons in heavy elements will be several times less than in substances with a small atomic number.

In conclusion the author wishes to express his profound gratitude to Prof. D. V. Skobeltzyn and Prof. I. E. Tamm for their valuable advice and discussion of the results obtained. A more detaled communication will be published in the Journal of Physics.

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PHYSIQUE

PENDULE INCLINÉ ET SON APPLICATION À L'ÉTUDE DU MÉCANISME MOLÉCULAIRE DE LA FRICTION EXTÉRIEURE DES CORPS SOLIDES

Par A. ACHMATOFF

(Présenté par A. F. Joffé, de l'Académie, le 11. VII. 1939)

La théorie moléculaire de la friction extérieure des corps solides en cas de surfaces pures et graissage imparfait se trouve à l'état primitif de son développement.

La présente Note préliminaire ne permet pas d'examiner la littérature correspondante (1). Il suffit d'indiquer que cette question exige de poursuivre les recherches.

Dans cet article nous exposons brièvement une nouvelle méthode d'étude des phénomènes de friction et de graissage imparfait, permettant d'obtenir, comme résultat statistique, directement de l'enregistrement des oscillations harmoniques amorties, une suite des valeurs caractérisant les phénomènes en question. Plus bas est également donnée la description des résultats obtenus par la méthode indiquée.

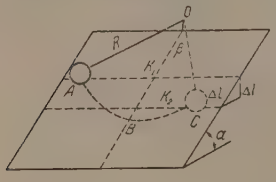

Fig. 1.

1. Le pendule incliné. Le nouvel instrument que nous proposons constitue l'ensemble d'un plan incliné et d'un pendule simple (réalisé par une petite boule métallique suspendue par un fil fin). Le couple de friction étudié est formé par une boule et un plan.

Il est évident que la boule placée sur une plaque inclinée (fig. 1) et fixée au bout d'un fil fin de soie (parallèle à la plaque) va effectuer, après avoir été écartée de son état d'équilibre OB, des oscillations amorties de roulement. Un tel instrument, que nous avons appelé pendule incliné, a été construit et essayé par nous dans les différentes conditions.

La composante normale N du poids de la boule varie avec l'angle d'inclinaison α de la plaque et reste constante en tous les points de la trajectoire de la boule, lorsque $\alpha = \text{const}$. Ceci permet pour les valeurs de α voisines de $\frac{\pi}{2}$ rendre N si petite qu'on puisse étudier la friction pour les charges très petites, de même que le phénomène d'adhésion (pour $N=0$). En remplaçant dans les mêmes conditions la boule par un curseur plan, il est possible d'étudier de même la friction de glissement. Indiquons que l'instrument permet également de faire varier la période de l'oscillation et le rayon de roulement.

Le pendule incliné* présente, par conséquent, le tribomètre le plus universel parmi ceux décrits jusqu'à présent dans la littérature.

2. La détermination des coefficients de friction de roulement δ et de glissement μ. L'étude du phénomène d'adhésion. La détermination expérimentale au moyen d'un pendule incliné des coefficients de friction de même que l'établissement d'un lien fonctionnel entre la friction et la vitesse exige la connaissance de la courbe de l'amortissement de ses oscillations.

Nous avons enregistré cette courbe par la méthode photographique. Les oscillations peuvent être projeter sur le plan de la pellicule de différentes façons. Nous n'en retiendrons que la projection à la pellicule photographique parallèle au plan incliné. La pellicule se déplace dans la direction OB (fig. 1). On obtient les courbes *2*, *3*, *4* et *5* (Fig. 2).

Il est évident que l'amortissement des oscillations harmoniques du pendule incliné, en négligeant, par suite de leur petitesse, la résistance de l'air et la perte de l'énergie pendant la torsion du fil fin de soie, sera entièrement causé par la friction extérieure R. Si l'on a R=const, les coefficients peuvent être déterminés très facilement.

En effet, la perte de l'énergie par le pendule pendant n oscillations doit être égale au travail des forces de friction sur le chemin S équivalent à n.

Pendant une demi-période, par exemple $\frac{T}{2}$, la perte de hauteur par le centre de gravité du pendule $(x_1 - x_2 = \Delta x)$ va être trouvée comme projection sur une verticale de la différence de longueurs $(l_1 - l_2 = \Delta l)$ mesurée sur la courbe expérimentale $\Delta x = \Delta l \sin \alpha$ (fig. 1). Alors on aura pour le coefficient de friction de roulement δ:

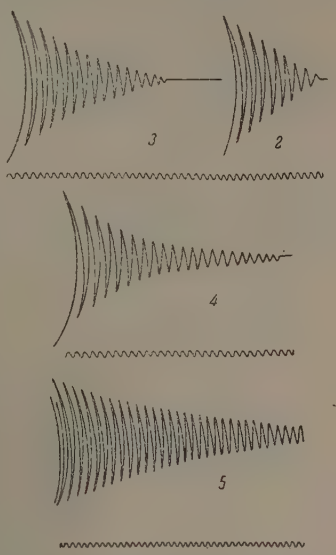

Fig. 2. *2*—surface polie et perfectement pure; *3*—la même surface couverte de plusieurs couches d'acide stéarique ($C_{18}H_{36}O_2$); *3* et *4*—surfaces perefectement pures, qui ont subi un traitement différent; *3*—fraisée; *4*—rabotée.

$$\delta = r \cdot \operatorname{tg} \alpha \cdot \frac{\Delta l}{S} \qquad (1)$$

où r est le rayon de la boule, α — l'angle d'inclinaison, S — l'arc ABC (fig. 1); Δl et S peuvent être trouvés d'après la courbe des oscillations, Δl — directement et S — par la valeur de sa projection $|k_1 + k_2|$ et la longuer R du pendule, car l'on a $k_1 = R \cdot \sin \beta$. On aura respectivement pour le coefficient de la friction de glissement μ:

$$\mu = \operatorname{tg} \alpha \frac{\Delta l}{R \cdot \operatorname{arc\,sin}\left(\frac{k}{R}\right)}. \qquad (2)$$

Les coefficients de friction, trouvés par la méthode décrite, satisfont aux valeurs données par des tables. Notons qu'en cas de surfaces pures les

* Nous avons commencé nos expériences par l'étude de l'amortissement des oscillations de roulement d'une boule sur la surface intérieure d'une sphère métallique. Le pendule incliné admet toute une série de modifications, par exemple, l'ensemble du pendule de Maxwell (volant, cylindre, etc.) avec un plan incliné.

coefficients de friction croissent considérablement. Par exemple, en cas de roulement de l'acier sur de l'acier le coefficient s'est trouvé égal à 0.032 cm (au lieu de 0.005 cm). Il est incontestable que la cause de cet accroissement des coefficients consiste en la diminution de l'écranement du champ de la phase solide pour les surfaces pures et ensuite en l'accroissement des forces d'adhésion (effet W. Hardy).

3. L'établissement au moyen d'un pendule incliné de la loi fondamentale de la friction dynamique. La forme analytique de la courbe des oscillations amorties d'un pendule incliné doit exprimer la loi fondamentale de la friction dynamique, à savoir, donner la force de résistance comme fonction de vitesse $F=f(v)$. La forme de cette fonction dépend des propriétés géométriques et physico-chimiques de la surface des corps (adsorption).

Lorsque $F=\text{const}$, la diminution de l'amplitude a lieu suivant la progression arithmétique. Pour $F=k\frac{dx}{dt}$ a lieu la loi logarithmique. Sont également possibles et très intéressants les cas intermédiaires où l'on a $F=k_1\left(\frac{dx}{dt}\right)^{\gamma}$, où $0<\gamma<1$. Enfin il est possible que l'on ait (²) $F=k_2\left(\frac{dx}{dt}\right)^2$.

4. L'influence de rugosité (le caractère de traitement) sur la forme de la courbe des oscillations amorties du pendule. Les expériences effectueés nous ont conduit aux résultats préliminaires suivants. En cas d'une surface polie (acier) très conciensieusement nettoyée l'amortissement est considérable et soumis à la loi $F=\text{const}$ (voir la courbe *2*). En cas de présence de rugosité reçue par suite de traitement mécanique de la surface (par une raboteuse, par la fraise, etc.), la friction dépend incontestablement de la vitesse $F=f(v)$ (voir les courbes *3* et *4*). Nous avons établi la forme de cette fonction et confronté les courbes obtenues au profil de la surface.

Nous supposons que le pendule incliné dans une de ses modifications peut avoir une application purement technique pour caractériser le traitement de la surface d'un corps solide *. Il suffira probablement de n'effectuer que les lectures visuelles de la variation de l'amplitude de l'oscillation.

5. De la statistique des ruptures des contacts élémentaires, considérées comme fondement de la théorie d'adhésion de la friction extérieure. Lorsqu'une boule roule sur un plan, les surfaces étant absolument polies et pures, le contact entre les deux surfaces doit être considéré comme pratiquement continu dans le temps.

La surface du contact S, égale d'après la théorie de Hertz à $S=\varkappa\cdot P^{2/3}$, où P désigne la pression, est soumise d'une part à la reconstitution continue (dans le sens du mouvement), et de l'autre côté à la rupture continue. La force de résistance est dans ces conditions constante et indépendante de la vitesse (fig. 2).

Le travail des forces de friction sur le chemin S va être exprimé, en cas d'une surface rugueuse, comme somme des actes élémentaires de contact des crêtes et des saillies avec la boule roulante. Il est évident que dans ce cas la force de friction dépend, par exemple, de la loi de distribution des contacts sur le chemin S, étant, bien entendu, une fonction de vitesse.

6. L'influence du graissage. Lorsqu'il y a sur une surface métallique polie un nombre croissant de molécules polaires (des acides gras), la loi de l'amortissement d'un pendule incliné change. Il suit de nos

* Ces travaux sont actuellement poursuivis par notre laboratoire.

expériences qu'en présence d'un nombre réduit de séries moléculaires dans la couverture d'adsorption du métal, par suite de l'hétérogénéité de la surface du corps solide, l'effet de l'écranement n'est pas le même pour différents endroits de la surface, d'où ils résultent des contacts discontinus. Lorsque l'épaisseur de la couche de graissage augmente, l'influence du glissement de ses plaques élémentaires se fait sentir d'avantage.

Dans une autre étude [3], terminée à présent, nous sommes arrivés à la conclusion que lors de la diffusion libre des molécules de la couche d'adsorption, aussi bien que dans les conditions de leur mouvement forcé, a lieu le déplacement cité plus haut des séries moléculaires des molécules orientées.

Il résulte des mesures du saut du potentiel de phases (électrique) que CH_3, surface d'une couche monotrimoléculaire, le plus solidement fixée, est le plan «principal» de glissement. Le déplacement, par courant continu aussi bien que par des endroits distincts (d'épaisseurs diverses) de la couverture lubrifiante, a lieu principalement suivant ce plan.

Les expériences préliminaires effectuées par nous au moyen d'un pendule incliné confirment ce point de vue. L'équation de Newton pour le courant laminaire est vérifiée pour une couche épaisse de graissage.

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PHYSIQUE

LA DIFFUSION DE COMBINAISON DES SOLUTIONS DE L'EAU PESANTE

Par G. S. LANDSBERG, membre correspondant de l'Académie, V. I. MALYCHEFF et V. E. SOLOVIEFF

L'étude de la diffusion de combinaison dans les mélanges montre que la perturbation de l'oscillation du groupe OH par des molécules voisines dépend en grande partie de la nature chimique des atomes constituant ces molécules.

Pour les solutions de l'alcool méthylique dans les dissolvants tels que CCl_4 et le chloroforme, les oscillations du groupe OH donnent une raie nette, c'est-à-dire, elles sont caractérisées par une fréquence déterminée, tout comme dans le cas des molécules isolées (le méthanol gazeux). Dans d'autres solutions les oscillations du groupe OH conduisent à la formation d'une raie plus ou moins élargie, indiquant la présence d'une perturbation visible venant des molécules du dissolvant.

La présence d'oxygène (et d'azote) dans les molécules des dissolvants conduit à la formation de raies assez larges, rappelant les raies du méthanol pur (on bien de l'eau). On est poussé à supposer qu'une action réciproque intermoléculaire beaucoup plus intense, observée dans le cas de l'alcool ou de l'eau, doit être expliquée par un lien hydrogène (ou bien du groupe OH), ayant lieu entre les groupes OH de quelques molécules. L'influence prédominante de l'atome de l'oxygène (ou de l'azote) indique également une action réciproque plus intense, pouvant avoir lieu entre le groupe OH et l'oxygène (azote) grâce au mécanisme, correspondant au lien d'hydrogène.

Il est intéressant, pour cela, d'étudier en quel degré il faut attribuer, en cas de liquides pures (méthanol et eau), l'élargissement de la raie OH à la présence de l'oxygène dans les molécules voisines, et quel est, d'autre part, le rôle de l'effet de résonance causé par la présence des groupes (OH) identiques dans les molécules à l'état d'action réciproque.

Nous avons, dans ce but, étudié les solutions de l'eau pesante (D_2O) et de l'eau ordinaire (H_2O) de même que celles de l'acétone $[(CH_3)_2CO]$. Les spectres de l'eau pesante, d'après de nombreux examens, sont caractérisés par une raie large, semblable à la raie OH que l'on observe dans l'eau ordinaire, mais déplacée dans le domaine des fréquences plus basses, ce qui correspond à la masse plus grande de deuterium.

Le maximum de la raie OD, donné par nos spectrogrammes, est la fréquence $\nu = 2535$ cm $^{-1}$, où la demi-largeur (d'après le microphotogramme) est voisine de 400 cm^{-1}. L'étude d'une solution de 3% de l'eau pesante dans de l'eau ordinaire a montrée, que les raies deviennent beaucoup plus étroites

et se déplacent vers les fréquences plus hautes, donnant le maximum pour $\nu = 2560$ cm^{-1} et la demi-largeur voisine de 200 cm^{-1}.

La solution de 3% de l'eau pesante dans l'acétone donne une raie encore plus étroite ayant le maximum $\nu = 2600$ cm^{-1} et une demi-largeur voisine de 130 cm^{-1}.

Ce résultat montre que, probablement, l'effet de résonnance joue un rôle important dans le phénomène de perturbation du groupe OD (ou bien OH). En effet, l'oxygène dans les molécules OD_2 et OH_2 doit avoir une configuration absolument identique d'électrons, et son action perturbatrice sur les oscillations de OD des molécules OD_2 doit être la même, le dissolvant de OD_2 serait-il de l'eau ordinaire ou de l'eau pesante. D'autre part, au point de vue de l'action réciproque de résonnance, il est essentiellement différent, les molécules de OD_2 seraient-elles environnées par les molécules de l'eau ordinaire ou de l'eau pesante. Probablement, l'action des molécules de l'eau ordinaire sur les oscillations de OD n'est pas très différente de l'action de l'acétone (et d'autres molécules contenant l'oxygène).

Il est possible qu'un élargissement un peu plus grand de la raie OD en cas de dissolution dans l'eau doit être attribué à la structure compliquée de l'eau, équivalente jusqu' à un certain degré du mélange de trois liquides aux distances moyennes intermoléculaires diverses (Bernal et Fowler).

Les expériences décrites ont été effectuées avec de l'eau pesante, aimablement mise à notre disposition des reserves de la Commission de l'eau pesante de l'Académie par le Prof. A. P. Vinogradoff, auquel nous exprimons nos sincères remerciements.

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ASTROPHYSICS

ON THE GRAVITATIONAL POTENTIAL ENERGY OF OPEN CLUSTERS

By V. A. AMBARZUMIAN, Corresponding Member of the Academy

The determination of the total gravitational potential energy of stellar clusters is of considerable interest for the theory of evolution of these objects (1). The knowledge of potential energy U (taken with reversed sign) permits to obtain the value of the whole energy H, since according to the virial theorem these quantities are connected by means of relation

$$H = -\frac{1}{2}U.$$

We can determine the numerical value of U if we know the density distribution in the cluster. At the same time the distribution of spatial density may be deduced from the distribution of surface density of masses within the projection of the cluster on the sky. This is achieved by way of the solution of Abel's integral equation. The distribution of surface density within the projection of the cluster on the sky can be found from the counts of stars of different absolute magnitudes, introduction of bolometric corrections and transition from bolometric absolute magnitudes to the masses of the stars. In this way N. S. Orlova (2) has determined the numerical values of U for eight open clusters.

However, this method is a very complicated one and can scarcely be applied to the clusters with relatively small number of members. We shall show that in the case of spherical symmetry of cluster (this assumption is necessary for the first method also) the quantity U can be expressed in a very simple form containing directly the surface density.

Let $\rho(r)$ be the space density, given as a function of distance r from the centre of the cluster. We can introduce a system of co-ordinates with its zero-point in the centre of the cluster and project all the stars of the cluster on one of the co-ordinate axes (say, the y-axis). The density distribution within such one-dimensional projection will be given by some function $\varphi(y)$. It is obvious that

$$\varphi(y) = 2\pi \int_y^\infty \rho(r)\, r\, dr.$$

For the mass $M(r)$ contained in a spherical volume with radius r around the centre we have

$$M(r) = 4\pi \int_0^r \rho r^2\, dr = -2 \int_0^r y \frac{d\varphi(y)}{dy}\, dy = 2 \int_0^r \varphi(y)\, dy - 2r\varphi(r).$$

The potential energy is equal:

$$U = G\int_0^\infty M(r)4\pi r\rho\,dr = -2G\int_0^\infty M(r)\frac{d\varphi(r)}{dr}dr =$$

$$= -4G\int_0^\infty \frac{d\varphi(r)}{dr}\left[\int_0^r \varphi(y)\,dy - r\varphi(r)\right]dr =$$

$$= 4G\int_0^\infty [\varphi(y)]^2\,dy + 2G\int_0^\infty r\frac{d[\varphi(r)]^2}{dr}dr = 2G\int_0^\infty [\varphi(y)]^2\,dy = G\int_{-\infty}^\infty [\varphi(y)]^2\,dy.$$

The obtained formula

$$U = G\int_{-\infty}^\infty [\varphi(y)]^2\,dy \qquad (1)$$

leads to a very simple method of calculation of U: it is necessary to divide the whole image of the cluster in a number of strips parallel to some arbitrary direction and count the sum of masses of the stars in each of these strips. Thus, we obtain the quantities $\varphi(y)\Delta y$, where Δy is the width of the strip. Taking the squares of these quantities, dividing by Δy, summing over all strips and multiplying by G, we obtain the numerical value of U.

The new method of determination of U has the advantage, that it can be applied to the poor clusters as well as to the rich ones.

We give below two examples of application of the formula (1) to open clusters (Coma Berenices and NGC 752) and the necessary details of calculation.

1. Coma Berenices. The distribution of masses in the projection on the sky was determined from the data given in a paper of Shajn. The masses of 15 stars which, according to Shajn ([3]), surely belong to the cluster were taken into account. The distribution of masses of 22 other stars which, according to Shajn, may possibly be members, too, was also added, but the masses of these stars were divided by 2. Thus, the total number of stars in the cluster in question was assumed equal to 26. Shajn states that the probable number of stars is equal approximately to 30. The masses of stars were computed from their bolometric absolute magnitudes. Kuiper's mass luminosity curve ([4]) was used. The bolometric corrections for known spectral types were taken from another work of Kuiper ([5]). The distance modulus was assumed equal to $4^m.3$.

2. NGC 752. The proper motions in this cluster were determined by Ebbinghausen ([6]). According to their proper motions all the stars were divided by him into a number of classes, with different probabilities of membership. We have taken into account only the stars of the first two classes of membership. The number of stars in other classes of membership physically connected with the cluster was assumed to be negligibly small. The distance modulus was taken equal to $8^m.0$. To the photographic magnitudes the bolometric corrections were added, and the colour indices subtracted from them. The bolometric corrections and colour indices were assigned in accordance with the spectral types. If the spectral class was unknown, it was assigned on the basis of the spectrum magnitude diagram of the cluster.

The results of calculation for both clusters are given in the table.

Cluster	Distance in psc	Number of members	Total mass	U in ergs
Coma Berenices	73	26	50	0.4×10^{44}
NGC 752	400	64	127	3.6×10^{44}

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PHYSIQUE TECHNIQUE

LE CHAMP ÉLECTROMAGNÉTIQUE D'UN OSCILLATEUR SPHÉRIQUE EXCITÉ PAR UNE FORCE ÉLECTROMOTRICE

Par A. G. ARENBERG

(Présenté par M. V. Shoulejkine, de l'Académie, le 6. VII. 1939)

1. Dans les Notes précédentes consacrées à la question d'émission électromagnétique de l'oscillateur de Hertz (1) ont été examinés les procédés différents de détermination de la puissance émise et de la résistance du rayonnement. On y a indiqué la nécessité de poursuivre les recherches des phénomènes d'émission électromagnétiques.

Dans le présent article nous allons considérer un champ électromagnétique créé par un oscillateur sphérique. Nous supposerons que les vibrations de cet oscillateur ont lieu sous l'influence d'une f. e. m. extérieure «superficielle», dirigée suivant ses méridiens*.

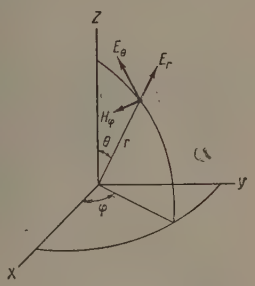

Fig. 1.

2. En cas de symétrie axiale $\left(\frac{\partial}{\partial \varphi} = 0\right)$, les équations de Maxwell pour les champs composants $\overline{E}$ et $\overline{H}$ (fig. 1) vérifiant la loi harmonique $e^{-j\omega t}$, sont de la forme

$$\left.\begin{aligned} jkE_\Theta &= \frac{1}{r}\frac{\partial}{\partial r}(rH_\varphi) \\ jkE_r &= -\frac{1}{r\sin\Theta}\frac{\partial}{\partial\Theta}(\sin\Theta \cdot H_\varphi) \\ jkH_\varphi &= \frac{1}{r}\left[\frac{\partial}{\partial r}(rE_\Theta) - \frac{\partial E_r}{\partial\Theta}\right] \end{aligned}\right\} \qquad (1)$$

où $k = \frac{\omega}{c}$ est le nombre ondulataire.

En introduisant la fonction auxiliaire $U(r, \Theta)$ telle que

$$rH_\varphi = jk\frac{\partial U}{\partial\Theta} \qquad (2)$$

on aura pour les composantes du champ électrique

$$E_\Theta = \frac{1}{r}\frac{\partial}{\partial r}\left(\frac{\partial U}{\partial\Theta}\right)$$

* Voir J. J. Thomson (2) qui considère le cas des vibrations propres d'un oscillateur sphérique, de même que les travaux de G. Mie (3) et P. Debye (4).

et

$$E_r = -\frac{1}{r^2 \sin\Theta} \cdot \frac{\partial}{\partial\Theta}\left(\sin\Theta \frac{\partial U}{\partial\Theta}\right). \qquad (3)$$

En substituant ensuite (2) et (3) dans la dernière expression du système (1), on obtient l'équation

$$k^2 U + \frac{\partial^2 U}{\partial r^2} + \frac{1}{r^2 \sin\Theta} \frac{\partial}{\partial\Theta}\left(\sin\Theta \frac{\partial U}{\partial\Theta}\right) = 0. \qquad (4)$$

Appliquons, comme l'on fait généralement, la méthode de Fourrier; l'on aura deux équations indépendantes, dont l'intégration permet d'exprimer la solution de l'équation (4) comme une série

$$U(r, \Theta) = \sqrt{r} \sum_{n=0}^{n=\infty} C_n \cdot Z_{n+1/2}(kr) \cdot P_n(\cos\Theta) \qquad (5)$$

où $Z_{n+1/2}(kr)$ est une fonction cylindrique de l'ordre $n + \frac{1}{2}$, $P_n \cos\Theta$ — une fonction sphérique de l'ordre n et C_n désigne une constante.

3. Nous introduisons dans la suite, d'après Debye [4], une fonction cylindrique $\xi_n(kr)$, telle qu'elle sera dans le cas des ondes «fuyantes» de l'oscillation ($r > a$) de la forme:

$$\xi_n(kr) = \sqrt{\frac{\pi kr}{2}} H^{(1)}_{n+1/2}(kr),$$

où $H^{(1)}_{n+1/2}(kr)$ est une fonction de Henkel du premier genre. En introduisant cette fonction dans l'expression (5) nous aurons:

$$U(r, \Theta) = \sum_{n=0}^{n=\infty} B_n \xi_n(kr) P_n(\cos\Theta). \qquad (6)$$

Désignons la f. e. m. extérieure (rapportée à l'unité de longueur de méridien)

$$E_e(\Theta) = E_{e_0}(\Theta) e^{-j\omega t}.$$

Bornons-nous au cas d'une sphère à la conductibilité idéale. On aura à l'aide des conditions limites pour E_Θ et $E_e(\Theta)$ et l'expression (3)

$$\frac{1}{r} \left| \frac{\partial U}{\partial r} \right|_{r=a} = \int_\Theta E_e(\Theta)\, d\Theta. \qquad (7)$$

Représentons ensuite, conformément au caractère du problème considéré, le membre de droite de cette expression comme développement en fonctions sphériques

$$\int_\Theta E_e(\Theta)\, d\Theta = \sum_{n=0}^{n=\infty} A_n P_n(\cos\Theta), \qquad (8)$$

où A_n est défini par la loi de distribution des f. e. m.

Alors, en déterminant la valeur de la constante B_n, l'on aura

$$U(r, \Theta) = \frac{a}{k} \sum_{n=0}^{n=\infty} A_n \frac{\xi_n(kr)}{\xi'_n(ka)} P_n(\cos\Theta) \qquad (9)$$

et par conséquent on pourra représenter les expressions (2) et (3) comme il suit:

$$\left.\begin{aligned} H_\varphi &= \frac{a\sin\Theta}{jr}\sum_{n=0}^{n=\infty} A_n \frac{\xi_n(kr)}{\xi_n'(ka)} P_n'(\cos\Theta) \\ E_\Theta &= -\frac{a\sin\Theta}{r}\sum_{n=0}^{n=\infty} A_n \frac{\xi_n'(kr)}{\xi_n'(ka)} P_n'(\cos\Theta) \\ E_r &= \frac{a}{kr^2}\sum_{n=0}^{n=\infty} A_n \frac{\xi_n(kr)}{\xi_n'(ka)} [2P_n'(\cos\Theta)\cos\Theta - P_n''(\cos\Theta)\sin^2\Theta]. \end{aligned}\right\} \quad (10)$$

La connaissance de la fonction $U(r, \Theta)$ permet de plus de résoudre la question de l'intensité du courant $I(\Theta)$ parcourant (par la bande sphérique de longueur $2\pi a \sin\Theta$) la surface de la sphère.

En effet, en substituant la valeur de H_φ (pour $r = a$) dans l'équation fondamentale de l'électromagnétisme

$$\frac{4\pi I(\Theta)}{c} = \oint H_\varphi dl,$$

on aura pour $I(\Theta)$ l'expression suivante:

$$I(\Theta) = \frac{ac\sin^2\Theta}{2j}\sum_{n=0}^{n=\infty} A_n \frac{\xi_n'(kr)}{\xi_n'(ka)} P_n'(\cos\Theta). \quad (11)$$

Plus loin nous allons nous servir de cette expression.

4. Pour illustrer les résultats obtenus, examinons le cas le plus simple, lorsque la distribution de la f. e. m. extérieure correspond au premier membre du développement (8), c'est-à-dire lorsqu'on a

$$\int E_e(\Theta)\, d\Theta = A_1 \cos\Theta$$

et par conséquent

$$E_e(\Theta) = E_m \sin\Theta$$

où

$$E_m = E_{m_0} e^{-j\omega t} = -A_1. \quad (12)$$

Alors, en nous servant de la relation connue entre les fonctions de Hankel et de Bessel (5), nous trouvons que l'on a:

$$\xi_1(x) = -\left(1 + \frac{j}{x}\right) e^{jx} \quad \text{et} \quad \xi_1'(x) = -\left(j - \frac{1}{x} - \frac{j}{x^2}\right) e^{jx}. \quad (13)$$

Substituons les expressions (12) et (13) dans la relation (10). On aura

$$\left.\begin{aligned} H_\varphi &= \frac{k^2 M_s \sin\Theta}{r}\sqrt{1 + \frac{1}{k^2 r^2}}\, e^{j(kr+\alpha)}, \\ E_\Theta &= \frac{k^2 M_s \sin\Theta}{r}\sqrt{1 - \frac{1}{k^2 r^2} + \frac{1}{k^4 r^4}}\, e^{j(kr+\beta)}, \\ E_r &= \frac{2kM_s\cos\Theta}{r^2}\sqrt{1 + \frac{1}{k^2 r^2}}\, e^{j(kr+\gamma)}, \end{aligned}\right\} \quad (14)$$

où

$$M_s = \frac{aE_m}{k^2\sqrt{1-\frac{1}{k^2a^2}+\frac{1}{k^4a^4}}}\, e^{-j(ka+\psi)};$$

$$\operatorname{tg}\alpha = -kr; \quad \operatorname{tg}\beta = \frac{kr}{k^2r^2-1}; \quad \operatorname{tg}\gamma = \frac{1}{kr} \quad \text{et} \quad \operatorname{tg}\psi = \frac{ka}{k^2a^2-1}.$$

Si l'on confronte ces expressions aux formules généralement connues des composantes du champ électromagnétique d'un dipôle élémentaire (6), il est facile de voir que le champ électromagnétique de l'oscillateur sphérique considéré correspond au champ d'un dipôle élémentaire (placé au centre de la sphère), dont le moment électrique est M_s.

5. Considérons maintenant la question de l'accordage d'un oscillateur sphérique excité par une f. e. m. extérieure distribuée sur sa surface de la façon indiquée («le premier harmonique sphérique»). Utilisons pour cela l'expression (11), dont la valeur absolue pour $n=1$ prend la forme

$$|I(\Theta)| = \frac{ac\sin^2\Theta}{2} E_m \sqrt{\frac{1+m^2}{1-m^2+m^4}} \qquad (15)$$

où $m=\frac{1}{ka}$.

Il est facile de montrer que $|I(\Theta)|$ admet un maximum pour $m_0=\sqrt{\sqrt{3}-1}$, ce qui correspond (pour $a=\text{const}$) à la longueur d'onde $\lambda_0 = 0.855 \cdot 2\pi a$*.

Nous voyons que la longueur d'onde «de résonnance» définie par cette relation ne coïncide pas avec la longueur propre de l'onde $\lambda_0 = 1.158 \cdot 2\pi a$, trouvée par J. J. Thomson (2) pour le cas des vibrations libres d'une sphère**.

L'écart obtenu des valeurs de λ_0 correspondant aux cas des vibrations libres et forcées de l'oscillateur rappelle en partie l'écart entre les grandeurs analogues qui ont lieu dans le contour oscillateur ordinaire de Thomson. Quant à la valeur assez grande de l'écart, il est probable que cela est dû à l'émission assez grande, au calcul de laquelle nous comptons consacrer une Note spéciale.

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* Il faut noter que, pour λ_0 donné, le champ électromagnétique de l'oscillateur sphérique, exprimé par la relation (14), varie à partir de sa superficie suivant la loi «d'une zone éloignée», dont la frontière conventionnelle est généralement définie par l'inégalité $kr \gg 1$.

** En effet, si pour $r=a$ on rend nulle l'expression (3) de E_Θ, on trouvera d'après (6) que ceci est possible pour $\xi_1'(ka)=0$, d'où la longueur propre de l'onde $\lambda_0 = \frac{4\pi a}{\sqrt{3}}$ et le décrement des vibrations $\gamma = \frac{2\pi}{\sqrt{3}}$.

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PHYSIQUE TECHNIQUE

SUR LA DISTRIBUTION DE L'ÉNERGIE D'UN OSCILLATEUR ÉLÉMENTAIRE

Par A. G. ARENBERG

(Présenté par M. V. Shoulejkine, de l'Académie, le 12. VII. 1939)

1. Nous avons montré dans la Note sur la résistance du rayonnement d'un oscillateur de Hertz * que si l'on détermine cette résistance R_Σ au moyen d'une intégration de flux d'un vecteur de Pointing $\overline{S}$ à travers une sphère enveloppant un dipôle, il suffit de ne considérer que l'influence du potentiel vectoriel $\overline{A}$. En même temps, la détermination de la valeur de R_Σ par la méthode des f. e. m. «induites» exige de tenir également compte de l'influence du potentiel scalaire φ.

Mais on peut montrer que si l'on intégrait le flux du vecteur $\overline{S}$ non suivant une sphère, mais sur un cylindre**, il faudrait, pour déterminer R_Σ, tenir compte des deux potentiels $\overline{A}$ et φ, ce qui donne les expessions coïncidant entièrement avec les expressions (15. I) obtenues plus tôt par la méthode des f. e. m. induites.

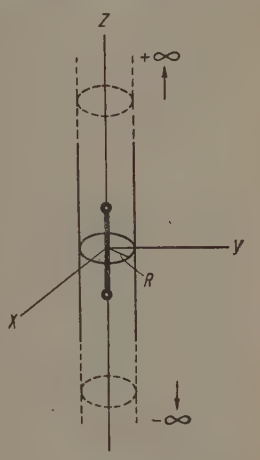

Fig. 1.

2. En effet, orientons l'oscillateur suivant l'axe z et considérons le vecteur de Pointing comme somme de deux termes $\overline{S_V}$ et $\overline{S_S}$ (dont le premier ne dépend que du potentiel vectoriel $\overline{A}$ et le second — du potentiel scalaire φ). Nous aurons alors pour la composante radiale du vecteur $\overline{S_V}$:

$$S_{VR} = -\frac{1}{4\pi}\left[\frac{\partial \overline{A}}{\partial t},\ \text{rot}\ \overline{A}\right]_R = -\frac{1}{4\pi}\frac{\partial A}{\partial t}\cdot\frac{\partial A}{\partial R} \qquad (1)$$

où $A = \frac{f'}{cr}$ et $R = \sqrt{x^2+y^2}$.

Puis, en intégrant la valeur moyenne de S_{VR} suivant la surface latérale d'un cylindre infiniment long (fig. 1) dans le cas des vibrations harmoniques, on aura, après le passage aux unités du système pratique, l'expression

$$P_{\Sigma V} = 60\pi^2\left(\frac{l}{\lambda}\right)^2 I_0^2 \text{ watts} \qquad (2)$$

* Voir C. R. Acad. Sci. URSS, XXIII, № 4 (1939). Les notations restent les mêmes. Les formules de cet article sont munies d'indice I.

** Ces calculs sont dus à R. Popoff.

ce qui correspond à la puissance émise par le dipôle, «empruntée» à son champ magnétique.

En définissant de la même manière la composante radiale du vecteur $\bar{S}_S$, nous aurons:

$$S_{SR} = -\frac{c}{4\pi}[\text{grad}\ \varphi,\ \text{rot}\ \bar{A}]_R = -\frac{c}{4\pi}\frac{\partial A}{\partial R}\left(\frac{\partial \Psi}{\partial R}\cdot\frac{z^2}{R}+\Psi\right) \qquad (3)$$

où $\Psi = \frac{f'}{cr^2}+\frac{f}{r^3}$.

L'intégration de la valeur moyenne de S_{SR} suivant la surface latérale du cylindre dans le cas des vibrations harmoniques nous conduira à l'expression

$$P_{\Sigma S} = -20\pi^2\left(\frac{l}{\lambda}\right)^2 I_0^2 \text{ watts} \qquad (4)$$

correspondant à la puissance «rendue» au champ électrique du dipôle.

Il est évident qu'en définissant à partir des expressions (2) et (4) les composantes de la résistance du rayonnement de l'oscillateur, dues aux potentiels $\bar{A}$ et φ, nous obtiendrons les formules (15. I):

$$R_{\Sigma V} = 120\pi^2\left(\frac{l}{\lambda}\right)^2 \text{ohm et } R_{\Sigma S} = -40\pi^2\left(\frac{l}{\lambda}\right)^2 \text{ohm}. \qquad (5)$$

La somme algébrique de $R_{\Sigma V}$ et de $R_{\Sigma S}$ conduit à la formule habituelle (6. I) donnant R_Σ.

3. Ensuite, il est facile de montrer que le vecteur de Pointing n'a suivant l'axe z qu'une seule composante:

$$S_{SZ} = -\frac{c}{4\pi}[\text{grad}\ \varphi,\ \text{rot}\ \bar{A}]_z = \frac{c}{4\pi}\frac{\partial A}{\partial R}\cdot\frac{\partial \Psi}{\partial R}\cdot z. \qquad (6)$$

On voit que la somme des projections des valeurs moyennes S_{SZ} et S_{SR} sur la direction du rayon-vecteur r est nulle, ce qui correspond aux résultats obtenus dans l'article cité plus haut. Il faudra de plus indiquer que l'intégration de la valeur moyenne de S_{SZ} sur un plan illimité perpendiculaire à l'axe de l'oscillateur donnera (pour $|z| > 0$) une grandeur égale à la moitié de toute la puissance émise.

La question des rôles des potentiels vectoriel et scalaire dans l'émission électromagnétique a été posée par M. V. Shoulejkine [1]. L'auteur tient à exprimer sa sincère reconnaissance pour ses conseils et son aide.

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CHEMISTRY

INFLUENCE OF ALKYL IODIDES UPON THE DECOMPOSITION OF CYCLOHEXANE

By L. I. BERENZ and A. V. FROST

(Communicated by S. S. Nametkin, Member of the Academy, 11. VII. 1939)

Jones and Ogg ([5],[8]) as well as other authors [([4]) and page 129 ([3])] have demonstrated that the thermal decomposition of alkyl halides leads to the ormation of free radicals as an intermediate stage:

$$RG \rightarrow R^- + G^-$$

From the point of view of the theory developed by Frost ([6]) different radicals cannot have the same reactivity. Our purpose was to study the accelerating action of different radicals upon the decomposition of hydrocarbons. As a source of radicals we decided to use alkyl halides. As an object for the study of the action of radicals cyclohexane was selected. This hydrocarbon decomposes very slowly ([7]) and its thermal decomposition, according to the theory of Rice, proceeds so that no chains are being developed, because the rupture of the ring leads to the formation of bivalent radicals. Therefore the action of radicals upon cyclohexane should be most noticeable.

The stream method under atmospheric pressure was used in our experiments. A spiral quartz tube immersed in a lead thermostat was used for a reactor. Cyclohexane or solutions of alkyl halides in cyclohexane were added at a constant velocity from a burette into the evaporator, from which the vapours passed over the reactor. The vapours coming out of the reactor were cooled and condensed. The gas was collected in a gasometer. The degree of decomposition was determined by the velocity of gas formation. Experiments were carried out at 580 and 600°C, the time of contact in the reactor being about 11 sec. Under such conditions the time of the complete decomposition of alkyl halides ([4],[5],[8]) amounts to fractions of a second, whereas cyclohexane decomposes only to the amount of 1—2%.

In the paper of Hinshelwood and Bairstow ([1],[2]) it was mentioned that iodine had an accelerating action on the decomposition of cyclohexane. Therefore, for comparison experiments were carried out in order to find out the influence of iodine upon the decomposition of cyclohexane.

The results obtained are given in the table. From the data obtained it may be seen that alkyl iodides have a stronger influence upon the decomposition of cyclohexane than the addition of iodine. It is also interesting to note that at first the increase of the amount of added iodine increases rapidly

the velocity of the decomposition reaction, but that an addition of iodine over 0.20% causes a decrease of the reaction velocity.

According to Frost ([6]), the velocity of the interaction of radicals with organic molecules should decrease in the following order: methyl, ethyl, sec.-propyl, tert.-butyl.

Primary propyl which decomposes into methyl and ethylene should produce a stronger action compared with sec.-propyl. Primary normal butyl which decomposes into ethyl and ethylene should act somewhat slower than the ethyl radical. Primary isobutyl which decomposes into methyl and propylene should act more rapidly than primary butyl.

The experiment showed that the action of alkyl halides did not confirm completely the predictions of the theory of Frost. Thus, ethyl iodide produced a somewhat lesser action than the addition of an equal amount of sec.-propyl. In all the other cases the relations found confirmed the deductions of the theory. Thus, methyl iodide produced the strongest action among the investigated alkyl iodides, and sec.-propyl iodide had a smaller influence than primary propyl iodide.

The work is being continued to bring more precision in the data obtained and to study the influence of butyl iodides upon the decomposition of cyclo-

No. of exp.	Substance added	$t = 580°C$, $\tau \approx 11$ sec.					$t = 600°$, $\tau \approx 13$ sec.				
		M% of the substance added d	Gas evolved			Bromine number of liquid product	No. of exp.	M%	Gas evolved		
			a[1])	b[2])	c[3])						
28	I_2*	0.0029	1.17	0.17	—	3.1					
34b	I_2	0.0033	2.0	1.0	—	4.6					
35	I_2	0.033	5.5	4.5	(136)	8.0					
34	I_2	0.17	7.8	6.7	39.4	12.6					
33a	I_2	0.34	4.5	3.5	10.3	8.56					
33b	I_2	0.34	4.8	3.8	11.2						
31a	I_2	0.9	2.5	1.5	1.6	6.5					
31b	I_2	0.9	2.7	1.7	1.9						
5	none	0.0	1.01	—	—		18	0.00	1.5	—	—
30	none	0.0	1.0	—	—						
10	CH_3I**	1.76	10.6	9.6	5.5		21	1.69	16.5	15	8.9
29	CH_3I	0.89	9.7	8.6	9.7						
9	C_2H_5I	1.33	5.6	4.6	3.5		20	1.33	11.4	9.9	7.5
27	C_2H_5I	0.75	4.8	3.8	5.1						
23a	$CH_3.CH_2.CH_2I$	0.90	7.2	6.2	6.9		16	9.19	11.3	9.8	8.2
23b	$CH_3.CH_2.CH_2I$	0.90	7.0	6.0	6.7						
26	$CH_3.CH_3.CHI$	0.91	6.1	5.1	5.6						
36	$CH_3I + Na$***	0.89	16.4	15.4	17.3						
38	Na***	—	7.9	6.9	—						

* In the experiments when iodine was the substance added, the per cent was calculated using the formula: $\frac{(\text{g of iodine}) \cdot 100}{127\ (\text{moles of cyclohexane})}$

** In the experiment when alkyl iodides were added, the per cent was calculated from the formula: $\frac{(\text{g of RI}) \cdot 100}{\text{mol. weight of RI (moles of cyclohexane)}}$

*** Sodium (3 g) was introduced directly into the coil.

1) a — total amount expressed in molar per cent referred to the amount of cyclohexane; 2) b — excess of gas due to the substance added in molar per cent referred to cyclohexane; 3) c — number of moles of the gas evolved due to the influence of the substance added and calculated per mole of this substance $= \frac{b}{d}$.

hexane. It is interesting to note that the attempt to increase the concentration of the radicals through the introduction of sodium into the zone of the decomposition of a mixture of cyclohexane and methyl iodide showed that sodium acted as a catalyst upon the decomposition of cyclohexane and that approximately its action was additive with that of methyl iodide (experiments 10, 29, 36 and 38).

As it can be seen from the above, it has been proved in this paper that alkyl iodides have a catalytic action upon the decomposition of cyclohexane.

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CHEMISTRY

CONTRIBUTION TO THE THEORY OF THE ORIGIN AND GROWTH OF METALLIC CRYSTALS WHEN DEDUCED FROM SALT SOLUTIONS

By P. D. DANKOV

(Communicated by Wl. A. Kistiakowsky, Member of the Academy, 25. VI. 1939)

§ 1. In most of the cases it is only after a more or less prolonged induction period (1) that metals are reduced from their salt solutions. In this second stage reduction usually goes on very violently, and the main mass of the metal is precipitated. The division of the process into two stages can be explained by the difficulty of nucleus formation (2) and the further facility of development of crystal centers already formed. However, up till now nobody has succeeded in drawing a more detailed picture of this phenomenon in face of the great theoretical and practical interest which belongs to the mechanism of the reduction process.

§ 2. In this article an attempt is made to construct a scheme of the elementary acts taking place in the phenomena of the reduction of metals from solutions of their salts. To this end it is necessary to pay a great deal of attention to the fact that, just as in many other phenomena [crystallization (2), catalysis (3), changes in hardness (4), changes in surface energy (5), etc.], the decisive rôle in the reduction of metals is played by the limit dimensions (6) of the particles of the condensed phase (drop, crystal), near which there is a transitional region. As we know (6), the intensity of the properties of a dispersed system in the case of a limit degree of dispersion has a maximum (3,4,5) which is the external manifestation of the fact that the condensed phase has limit dimensions. For continuous systems the limit thickness should play an essential part; in passing over to the latter a number of properties of the body change pronouncedly. An enormous number of papers (7) examining the properties of thin metallic films mention the existence of a limit thickness for the metal layer, after which further decrease in thickness results in a quick change in properties which come to show considerable departure from the normal ones (conductivity, magnetic properties, photoeffect, etc.). The clear-cut manifestation of special properties in metals in thin layers is due to a considerable degree to characteristic features of the metal state, which is distinguished by high mobility of the valency electrons within the metallic body. As has already been mentioned in the work of De-Boer and Kraak (8), the transitional state of the metal (in the region of layers below the limiting thickness) is determined by partial connexion of the valency electrons when the metallic atom is not well enough surrounded by other atoms of the metal. The more «neighbours» each metallic atom has in the condensed system, the more the potential

barrier which keeps the electron from passing from one atom to another is lowered. In a normal piece of metal the number of atoms in unit volume is very great, and the potential barriers are so greatly lowered that they cannot seriously hamper the motion of the electrons (the electron gas). Such a notion, of course, assumes the existence of a well enough expressed transitional state, which has been recorded in many experiments with thin layers ([7]).

Doubtlessly, it is possible also to extend the correlations examined to the system of metallic atoms which forms when metals are reduced from solutions of their salts. As will be seen from the following, the capability of electrons to change place freely, which increases together with the size of the metallic particle, plays an essential part in the mechanism underlaying the second stage of reduction of the metal.

However, in order to understand the first stage of reduction—the formation of nuclei—supplementary considerations are necessary. As Volmer ([2]) noted, it is hard to expect that the nucleus will form at the expense of fluctuation even in the case of the simple process of the formation of a drop from apour. In our case, which is accompanied by chemical changes, it is even harder to expect this. Therefore it is necessary to give preference to the point of view, according to which the nucleus does not form spontaneously: the nucleus develops on ready-made surfaces, which are capable of orientating the evolving ions—atoms into a system close to the metallic state. Indeed, the facts observed by us ([1]) of the pronounced decrease of the induction period during the reduction of platinum under the influence of dust particles from the air, speak convincingly for the mechanism of the formation of nuclei on the surface of a solid body. The nature of the dust particles and the nature of their orientational action have not yet been found out. However, it has been shown more than once, that in cases when the metal vapours condense ([9]), the crystal surfaces have a well-expressed orientational influence. It is impossible, of course, to identify the phenomenon of condensation of metal vapours with the process of deposition of the metal when reduced from its salt solutions. Nevertheless, the similarities of these processes catch the eye. Besides, in our laboratory's study mentioned above it was observed that the initial stage of platinum deposition goes on according to approximately the same probability scheme, as during the condensation of metallic vapours ([10]). Both during the condensation of vapours and during the reduction process the essential part is played by the «waiting time» which is the inverse value of probability. In both cases there is a sharp break in the «waiting time»—saturation curve (in vapour condensation the saturation factor was temperature of the surface; in reduction, the concentration of the reagents).

Of course, these processes go on under essentially different conditions. In reduction the deposition of the metal (Me) develops as a result of the metal ions (Me^{n+}) accepting electrons (Θ), freed by the reducing agent (Red^{n-}) in its passing into the oxidized form (Ox) according to the following scheme:

$$1.\ (Red^{n-}) \rightarrow (Ox) + n\Theta$$

$$2.\ \frac{Me^{n+} + n\Theta \rightarrow Me}{Me^{n+} + (Red^{n-}) \rightarrow Me + (Ox)}$$

Evidently, the phenomenon of condensation depends not only upon the affinity of the metallic ions with the surface (the adsorption energy), but also upon a favourable combination of cases of electrons being transferred to the ions (the activity of the reducing agent). The processes of adsorption of the l i m i t number of ions and of the transference of electrons onto them should be localized at the same place on the surface. It is with this last fact that

the difficulty met with during the formation of the nucleus is connected. It must, however, be noted that in describing this phenomenon correlations, analogous for cases of condensation of metal vapours in a vacuum on a surface (dwelling times, adsorption heats, etc.), should be taken into account.

In our case the transitional state of the metal nuclei, which form as time goes on, continues until their dimensions increase enough for noticeable mobility of electrons to begin within the metallic particle. After this the mechanism of deposition of the metal changes: the second, considerably facilitated stage of the process begins. This is connected with the fact that when the electrons within the formed nucleus are mobile, localization of the ionic processes in one place is no longer necessary. Indeed, similarly to a macroscopic electrode the metallic particle takes on a redox potential (ε_{Red}), corresponding to the electrochemical equation

$$\varepsilon_{Red} = \varepsilon^{\circ}_{Red} + \frac{RT}{nF} \ln \frac{Ox\,[H^{+}]^{n}}{Red^{n-}}$$

where $\varepsilon^{\circ}_{Red}$ is the normal potential; R, the gas constant; T, the absolute temperature; n, the valency of the metallic ion; F, Faraday's number; Ox, the concentration of the reducing agent in the oxidized form; Red, the concentration of the reducing agent; $[H^{+}]$, the concentration of hydrogen ions.

However, the presence of metallic ions capable of accepting freed electrons affects the electrode potential of the particle (depolarization). The more quickly the metallic ions are discharged, the more positive the potential. The discharge takes place ([11]) along the line of growth (electrocrystallization) which represents a moving cathode; the rest of the particle's surface plays the part of the anode.

The metallic ions get considerable advantages in passing into the metallic state after the formation of a nucleus with the high electronic mobility characteristic of metals. Due to this, the reduction of the metal and the corresponding oxidation of the reducing agent can be divided spatially and fixed in various parts of the nucleus' surface. It is clear, this possibility is much greater than the probability of the process as a whole taking place, since the elementary acts of accepting electrons (by metallic ions) and giving them away (by the reducer) can be realized by way of the metallic particle. Fulfilling such a double function the particle shows an approximately equal increase in size in all directions, since the concentration of the reagents is the same in all directions. Even deposition of the substance per unit surface of the particle results in the velocity of the process quickly increasing for the whole particle, since its surface grows in proportion to the square of the increment of the particle's radius. These facts determine the violent course of the process observed during the second stage of reduction following the induction period ([1]).

This point of view is borne out by observations described in the work of Jevstropyev and Samartzev ([12]). A platinum electrode submerged in a solution of silver nitrate and cane sugar (which has reducing powers) behaves in the following manner. Its potential decreases in about one or two minutes to a certain negative value; then it passes its minimum and returns to more positive values. Evidently, after five minutes the potential of the platinum electrode reaches a value which corresponds to the redox potential of a mixture of silver nitrate and cane sugar solutions, and keeps it for a long time. This interesting observation shows that the introduction of a metallic body into a solution with a tendency to reduce the metal, makes it quickly assimilate the reducing tendency of the reducing agent (e. g. cane sugar, formaldehyde, etc.), accepting electrons, and only after the latter have accumulated in sufficient quantity does it begin to react actively with silver ions

(or other metallic ions, e. g. Pt^{++++}) which are deposited on the electrode, forming a nucleus which is now capable of growing at the normal redox potential in accordance with the electrochemical scheme proposed above.

We wish to call attention to the fact that the variation of the «test» electrode's potential described, which was observed in the work of Jevstropyev and Samartzev, is similar in many details to the potential variation in the initial stage of the electrocrystallization of silver and cadmium, described by the same authors. Here it should be added that in the work of Kohlschütter ([13]) mention is made of the fact that silver is chiefly deposited on the platinum surface, if the latter is submerged in a reducing solution of silver oxide.

§ 3. In concluding we shall summarize the above schemes of the formation and growth of metallic crystals which form during reduction from solutions.

Metal nuclei are formed on solid surfaces in the solution (e. g. dust particles, the walls of the vessel, metallic surface); this process is similar to the primary stage of condensation of metallic vapours on the surfaces of a solid body. The nucleus passes through various transitional states corresponding to a partial lowering of the potential barrier, a condition for the electrons to be transferred from one metallic atom to another. If here the nucleus reaches such dimensions that the electrons within it have considerable mobility, the deposition of the metal becomes very much easier, because the process which consists in the electrons being given off by the reducing agent can be spatially separated from that, in which they are taken up by metallic ions. The electrochemical mechanism of the process of the metal depositing on the nucleus as a microscopic electrode becomes possible.

Thus, the reduction of a metal from solutions may be a typical representative of the colloido-chemical phenomena classified by Wl. A. Kistiakowsky([14]).

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CHEMISTRY

BROMINE CATION AS A BROMINATING AGENT

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While investigating the bromination kinetics of olefinic compounds in aqueous solution we have found the hydrogen ion to accelerate the reaction between *m*-anisolsulfonate and hypobromous acid very considerably. For slight alkaline solutions the kinetic equation is valid:

$$-\frac{d\,[\mathrm{HOBr}]}{dt} = k_2 A\,[\mathrm{HOBr}] \qquad (1)$$

where k_2 is 0.12 at 0°C (A being the concentration of *m*-anisolsulfonate). The values of k_2 at higher concentrations of the hydrogen ion are given in Table 1.

Table 1

Acid added	$10^3\,[H^+]$	k_2	$10^{-3}\frac{k_2}{[H^+]} = 10^{-3}k'$
HNO_3	0.911	8.75	9.6
HNO_3	2.296	18.0	7.84
H_2SO_4	4.738	38.5	8.13
H_2SO_4	9.392	78	8.3
HNO_3	10.01	71	7.1
HNO_3	16.32	109	6.7
H_2SO_4	16.44	115	7.0
HNO_3	34.76	186	5.35
HNO_3	90.04	480	5.33
			7.3

The values of k_2 in Table 1 have largely been derived as means of many experiments, in which A was 3.4—10.8 millimoles per litre, and the concentration of HOBr was 1.9—4.2 millimoles per litre. The concentration of pH is assumed to be equal to the equivalent concentration of the acid added. The temperature in the experiments was 0°.

In the last column of the table there are given the values $\frac{k_2}{[H^+]} = k'$. They are roughly constant: pH increasing 100 fold, the departures from the mean are no more than 0.3 of this. The coefficient k' appears to go down as pH goes

up, some additional factors coming probably into play here. In the first approximation the velocity of the reaction is proportional to pH. Therefore equation (1) can be substituted with

$$-\frac{d\,[\mathrm{HOBr}]}{dt} = k' A\,[\mathrm{HOBr}]\,[\mathrm{H^+}]. \qquad (2)$$

This form of the kinetic equation suggests that the bromination proceeds through the bromine cation, since the product $[\mathrm{HOBr}]\,[\mathrm{H^+}]$ is the measure of the formation of bromine cation according to the equilibrium

$$\mathrm{HOBr} + \mathrm{H^+} \rightleftarrows \mathrm{Br^+} + \mathrm{H_2O}. \qquad (3)$$

No data on bromine cation are available, except for the kinetical ones. As an ion with an incomplete electronic shell, it must be hydrated in aqueous solution to $[\mathrm{BrOH}]^+$ resonating with

$$\overset{\mathrm{Br}}{\mathrm{HOH^+}},\quad \overset{\mathrm{Br^+}}{\mathrm{HOH}},\quad \overset{\mathrm{Br}}{{}^+\mathrm{HOH}}$$

We have attempted to determine the concentration of bromine cation in aqueous solutions of hypobromous and nitric acids by the method of the electric conductivity. As equation (3) shows, the formation of bromine cation is connected with the disappearance of the very mobile hydrogen ion. Therefore, the specific conductance must lower, if bromine cation is forming. However, our experiments have not revealed any difference between the specific conductance of nitric acid diluted with water or with equal amount of hypobromous acid solution. The concentration of bromine cation is thus too small to be detected by the method used. This method allows only to calculate the maximum value of pH. We would, indeed, have observed the alteration of specific conductance if it had reached 0.15% of the measured value. In one experiment the concentration of HOBr was 0.0236 moles /l and that of HNO_3 was 0.0203 moles/l. Hence

$$\left(\frac{[\mathrm{Br^+}]}{[\mathrm{H^+}]\,[\mathrm{HOBr}]}\right)_{\max} = K_{\max} = \frac{0.00003}{0.0236 \times 0.0203} = 0.063.$$

Replacing $[\mathrm{H^+}]\,[\mathrm{HOBr}]$ in equation (2) by $\frac{[\mathrm{Br^+}]}{K_{\max}}$, one may calculate the value $(k_2)_{\max} = \frac{k'}{K_{\max}}$ in the kinetic equation

$$-\frac{d\,[\mathrm{HOBr}]}{dt} = k_2 A\,[\mathrm{Br^+}].$$

Evidently, $(k_2)_{\max} = \frac{7300}{0.063} > 110\,000$.

If instead of nitric or sulfuric acid one adds hydrobromic or hydrochloric acid to the mixture of *m*-anisolsulfonate and hypobromous acid, the reaction takes another course, owing to the formation of bromine and bromine chloride acting as independent brominating agents. The corresponding data will be exposed elsewhere. In this paper we shall only note that the bromine cation is the most active among brominating agents in aqueous solution.

In Table 2 are summarized the values of velocity constants k_2 of bromination of *m*-anisolsulfonate found by the same method and under the same conditions as for bromine cation.

Table 2

Brominating Agent	BrOH	Br_2	BrCl	Br^+
k_2	0.12	80	43 000	>110 000

This series of activity agrees perfectly with the principles of electronic theory of halogenation ([1]). The activity of any brominating agent BrX is evidently determined by its tendency to polarize into $Br^+—X^-$. Therefore, the series ends naturally with bromine cation, reaching the limit in the degree polarization.

Experimental. Sodium-*m*-anisolsulfonate was synthesized from methanilic acid through the diazocompound and *m*-anisolsulfochloride and obtained as a very pure preparation. Aqueous hypobromous acid was prepared by vacuum distillation of bromine water treated with silver phosphate ([2]). The experiments were made in an ice thermostat provided with a mechanical stirrer. The course of the reaction was followed iodometrically from the decrease of bromine titre in the solution. Titrations were made by means of cockless apparatus of microvolume analysis ([3]). For one experiment 20 ml hypobromous acid and 20 ml *m*-anisolsulfonate solution were taken. The stability of hypobromous acid under the conditions available (except *m*-anisolsulfonate) was controlled by parallel experiments. The data of three typical experiments are given by way of example below (Table 3).

Table 3

Exp. 72			Exp. 58			Exp. 72		
$A_0 = 0.005405$ $(HNO_3) = 0.000911$			$A_0 = 0.005822$ $(HNO_3) = 0.00822$			$A_0 = 0.005405$ $(HNO_3) = 0.000911$ $(HCl) = 0.00001205$		
t	10^3 [HOBr]	k_2	t	10^3 [HOBr]	k_2	t	10^3 [HOBr]	k_2
0	4.032	—	0	1.884	—	0	4.032	—
7	3.08	7.86	2	0.575	119	3	2.815	25.3
15	2.265	8.78	3	0.34	119	7	1.915	25.7
30	1.47	8.90	4	0.23	114	12	1.30	26.0
70	0.59	9.46			117	20	0.815	25.4
		8.75						25.6

An electronic valve apparatus, including a generator and an amplifier, was used to measure the conductivity of mixtures of hypobromous and nitric acids. The temperature in the experiment was 0°. The readings of minimum on the Kohlrausch bridge was as precise as to 0.1 mm.

The maximum concentrations used are shown above. Other experiments were made with solutions containing about 0.005 mol. HOBr and HNO_3. In all experiments the observed conductivity value was identical with that of control solution, where hypobromous acid was substituted with water.

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CHEMISTRY

RATE OF ENZYMATIC HYDROLYSIS OF PROTEINS

By I. A. SMORODINTZEV and V. P. ZHIGALOV

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It is generally claimed that the enzymatic hydrolysis of proteins proceeds very slowly, and after several weeks or even months have passed, the degree of completeness is not attained which under the action of acids is reached as early as in 48 hours ([1]). The erroneousness of this opinion was unmistakably demonstrated by our experiments. The splitting up of proteins under the influence of proteolytic enzymes is most intensive from its very start and in 1.5—3 hours a high degree of completeness is reached which increases but slightly during the subsequent hours. If hydrolysis proceeds under the consecutive action of pepsine, pancreatine and erepsine, it is much more complete and the decomposition of proteins is by far more rapid than in the case of boiling concentrated hydrochloric acid. In the experiment the pepsine, pancreatine and intestinal erepsine were made to act in succession on a high quality cattle meat. The degree of protein breakdown was estimated from the amino-nitrogen by means of van Slyke's apparatus on the basis of a raw meat aliquot. The pH was measured electrometrically. The results of some typical experiments on meat protein digestion are referred to in the table by way of example. Liquid coefficient, 1 : 8; temperature of steeping, 37°C; length of digestion, 30 min.

0.01% pepsine			2% parcreatine			1% erepsine		
pH	Amino-nitrogen in %	Amino-nitrogen to total nitrogen	pH	Amino-nitrogen in %	Amino-nitrogen to total nitrogen	pH	Amino-nitrogen in %	Amino-nitrogen to total nitrogen
1.60	0.38	10.3	8.5	2.0	57.0	8.2	3.1	89.0
1.71	0.40	11.4	8.2	2.4	69.0	7.9	3.0	87.7
Average		10.8			63.0			88.3
% of amino-nitrogen in total nitrogen		13%			66%			100%

Taking for 100 the total quantity of amino-nitrogen liberated on hydrolysis, we will find 13% of it to be liberated in 30 min. by a 0.01% solution

of pepsine. Another 66% get free during the further 30 min. under the action of pancreatine on the same substratum at pH=8.5. The 21% which remain are the share of the erepsine. The result after 1.5 hour is a meat practically free from amino-nitrogen, while in the case of concentrated hydrochloric acid three hours are required to split off only 30% of amino-nitrogen, i. e. three times less an amount.

Conclusions

1. The extent of protein breakdown in meat under the action of pancreatine and erepsine is not affected by either degree or duration of the preceding hydrolysis by pepsine.

2. The treatment of the proteins of muscles by pepsine is an indispensable preliminary to the action of pancreatine.

3. Pepsine (in 0.01% concentration) splits 10—15% of amino-nitrogen from the protein during 30 minutes.

4. If meat had suffered the action of pepsine, the amount of amino-nitrogen liberated by pancreatine is 5—6 times that liberated by pepsine.

5. The amount of amino-nitrogen isolated during 30 min. by the erepsine, when the latter comes after the pepsine and pancreatine, is twice that isolated by the pepsine.

6. If pepsine, pancreatine and erepsine act in succession, the hydrolysis of proteins is three times more intensive compared to boiling with concentrated hydrochloric acid.

7. If the hydrolysis of meat is effected by the action of enzymes, the amount of amino-nitrogen isolated during 1.5 hour is three times that isolated during 3 hours by boiling with concentrated sulphuric acid.

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CHEMISTRY

FORMATION OF PROTECTIVE CRUST ON SODIUM CHLORIDE ON ITS DISSOLVING IN SODIUM SULPHATE SOLUTIONS

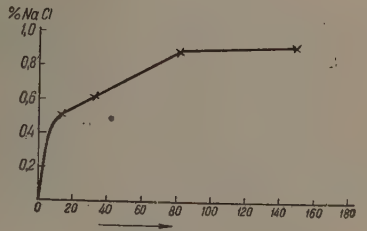
By A. V. NIKOLAEV and A. G. CHELISHCHEVA

(Communicated by N. S. Kurnakov, Member of the Academy, 29. VI. 1939)

While studying the rate of sodium chloride solution in Na_2SO_4, the authors have unexpectedly observed a tenardite crust to form on the dissolving surface. The geometrical surface of NaCl (polished) was 19.2 cm^2; four cubes weighing together 6.8 g were taken. They were placed into a vessel containing 50 g of mirabilite. The experiment was carried out with stirring. The solution of NaCl passed through three stages, as will be seen from figure and Table 1. The process started with the fusion of mirabilite and NaCl was dissolving in the melt. Further on the rate of solution decreased and it practically came to an end in 80 min.

Table 1

Time	% of NaCl in the melt
12 min.	0.51
30 »	0.60
1 h. 20 »	0.89
2 » 30 »	0.92



Time in min.

The cubes removed from the solution at the expiration of the experiment were found to be covered with a compact crust of tenardite. Naturally enough, this crust had stopped dissolution. This phenomenon was quite unexpected and we deemed it wise to verify it by a series of experiments. The results of the latter are given in Table 2 (50°C, experiments were carried out with stirring).

In all experiments except the last the crust of tenardite was continuous all over the surface of NaCl. A portion of the crust from one of the samples was analyzed (with NaCl, certainly) and it gave 56.17% of Na_2SO_4. When sodium chloride was reduced to fine fragments, it dissolved readily and without impediment in mirabilite, provided that the chloride was added to the solution and not the other way round. Of a number of similar experiments only four are referred to here by way of example (Table 3—75°C, 21 g of NaCl was taken for 100 g of mirabilite; experiments were carried out with stirring).

Table 2

Exp. No.	Surface	Amount of melt obtained from $Na_2SO_4 \cdot 10H_2O$ in g	Time	% of NaCl in the solution
1	10.7 cm²	150	5 min.	0.04
			15 »	0.07
			30 »	0.08
			1 h.	0.12
			2 »	0.11
2	2 crystals (cubes, 1 cm³ each)	62	5 min.	0.39
			15 »	0.46
			1 h.	0.53
			3 hrs 40 min.	0.53
3	2 crystals (cubes, 1 cm³ each)	62 g and 3 g of water added	10 min.	0.28
			30 »	0.49
			1 h.	0.57
			3 »	0.62
4	22.65 cm²	131.5 g and 2 g of water added	5 min.	0.56
			15 »	0.54
			30 »	0.55
			1 h.	0.56
5	22.0 cm²	100 g of distilled water	3 min.	4.79
			10 »	11.21
			30 »	13.15
	All NaCl dissolved			

Table 3

Series I			Series II		
Crystals of NaCl were added to the melt of mirabilite			Melt of mirabilite was added to the crystals of NaCl		
Time	% of NaCl in the melt		Time	% of NaCl in the melt	
	Exp. I	Exp. II		Exp. I	Exp. II
2 min.	23.63	23.93	2 min.	11.52	3.65
5 »	24.75	24.78	5 »	17.92	4.62
10 »	25.03	25.08	10 »	20.70	7.33
20 »	25.01	25.12	20 »	24.58	10.88
1 h.	25.10	25.15	1 h.	25.20	15.37
			2 »	25.14	19.62

The results summarized in Table 3 and corroborated by those of other numerous experiments show that well reproducible data are obtainable by adding the crystals of NaCl to the melt.

With the reverse order of addition different data were obtained in each of the experiments. Mention needs to be made of the fact that in the first series the equilibrium was reached in 1 hour in experiment I and was not attained even after 2 hours in experiment II. It will be obvious that the protective crust of tenardite was an obstacle in these cases too.

Another 7 experiments were made for studying the composition of the solid phase by the method of Shreinemakers. They were conducted at 50° C with stirring of the mixture of solid NaCl and $Na_2SO_4 \cdot 10H_2O$. The amount of NaCl per 100 g of mirabilite was 7.5 g (1 exp.), 10 g

(2 exp.) or 15 (14 exp). In other words, NaCl was taken always in lower quantity than that required for attaining the point of joint saturation of NaCl and Na_2SO_4.

In six experiments the time of sampling ranged from 2 to 6 hours and was 20 min. in one case only. It was found that in 4 cases out of 7 the tenardite contained from 1 to 7% of NaCl. Particularly interesting is the fact that appreciable amounts of NaCl were discovered in the case of 7.5 g (3%) and 10 g (7%) of NaCl. These latter facts show that NaCl will not pass entirely into solution on joint melting, though it might do so according to the equilibrium diagram data.

Some industrial experiments on solution of NaCl in melted mirabilite were performed at the works of Salts and Chemicals Ltd, Canada, while verifying the patent by Ide and Handcock (1). During these experiments vacuum (fine) sodium chloride had been added to the melt, but nevertheless the composition of tenardite obtained was beyond the limits of the Soviet standard (allows 1% of NaCl).

Undissolving residue	— 0.28%
$NaHCO_3$	— 0.31%
$CaSO_4$	— 1.22%
$MgSO_4$	— 0.50%
NaCl	— 3.04%
Na_2SO_4	—93.00%
Total	—98.35%

It will be apparent that the solution of NaCl will never be complete.

Mechanism of Formation of the Protective Crust. For the process of dissolution Nernst and Brunner assumed the formation of a film of saturated solution at the surface of the salt. The diffusion to the inner parts of the solution goes on from this film. But NaCl supplanting Na_2SO_4 from its solutions (2), solid tenardite has to be deposited. This process of displacement must be most intensive near the surface of sodium chloride. This circumstanse creates conditions for the crust to form on the surface. Now there is a tendency to supersaturation in sodium sulphate and the heavier supersaturated solution is apt to leave the surface and deposit tenardite away from the latter. This might account for the easiness of crust formation on large samples of NaCl, on the one hand, and for the unhindered dissolution of fine NaCl, on the other.

The influence of the order of addition can be explained on the basis of these assumptions, too. When solid NaCl is added to a solution of mirabilite, the precipitating crystals leave the layer of supersaturated solution and the crust is not formed. This is the case of a normal and reproductible solution. In the reverse case when the solution of Na_2SO_4 is added to sodium chloride, the supersaturation is extended throughout the space between the crystals and therefore the deposition of tenardite takes place on the surface of the crystals. The supersaturated solution seems to have a very short life, for a stirrer was always set in motion immediately after the addition of the melt.

The phenomena observed by the authors have a practical interest. When equilibrium is studied in salt systems, the method of repeated decantations of the solution into fresh portions of solid phase is being made use of. A presence of protective crusts explains this method quite easily. At the same time, according to our data, the solution should not be added to fresh portion of solid phases, but, on the contrary, the solid salts should be added to the stirred solution.

Many workers in sulphate production have now taken interest in the joint fusion of sodium chloride and mirabilite. The fact stated above should be taken into consideration in carrying out the experimental works. The following points are especially to be emphasized: a) fine crushing, b) good mixing during fusion, c) the prescribed run of the technological process must be thoroughly followed and especially the order of addition of the reagents, d) the standard for anhydrous sulphate obtained in this way probably needs revision.

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CHEMISTRY

PERIODIC ELECTROLYTIC DEPOSITIONS OF THE ALLOY ZN-CD FROM SULPHATE BATHS

By P. F. MIKHALEV

(Communicated by Wl. A. Kistiakowsky, Member of the Academy, 15. VII. 1939)

The application of the electrolytic alloy Zn-Cd produced from sulphate baths in protecting various metallic details from corrosion is of great practical and theoretical interest. There are several works in literature on the production of such an alloy from cyanide baths ([1],[2],[3]), as well as sulphate baths in the presence of various organic and colloidal admixtures ([4]). In this publication we give the results of a study of the process of periodic electrolytic deposition of the alloy from sulphate baths in the presence of admixtures.

Periodic variation in the cathode potential and layered deposition in electrolysis were studied as far back as 1910 by Macfadyen ([5]), then by Grube and Russe ([6]), Morre ([7]) and Mayer and Phillips ([8]). The latter studied the periodic variation in cathode potential during the electrolytic deposition of copper from cyanide baths and from sulphate baths in the presence of 0.1 g per litre of the foreign cations Cd and Pb. The cathode potential varied within 50 mV. The oscillation period was about 6 minutes.

Our study bears a somewhat different character from all those mentioned above, since here the periodic variation in cathode potential is concomitant to a layered deposition of Zn and Cd and also to a periodical change in the tension on the electrodes and in the current strength.

The alloy was deposited electrolytically from a bath of 150 cm^3 capacity. The cathode was a copper plate 6 cm^2, and the anode was a platinum plate 5 cm^2. The bath was kept at a room temperature 18—19°. All the salts used (brand of Laboratory Equipment Centre, USSR) were recrystallized several times each, depending on the pureness of the initial products. The coffein and cadmium sulphate used were Kalbaum brands. The cathode polarization was measured after the compensation method by means of a Raps potentiometer. The composition of the sulphate bath used was as follows: $ZnSO_4 7H_2O$—340 g, $Cd(SO_4)_3 H_2O$—16 g, $Al_2(SO_4)_3 18H_2O$—20 g, pH—3.2 g.

Fig. 1 shows how the change in the potential of the cathode during the process of electrolytic deposition of the alloy Zn-Cd from this bath without organic and colloidal admixtures is related to the change in current.

From Fig. 1 it is evident that with a current no less than 10.5 mA, and a tension on the electrodes no more than 2.6 V the more noble metal alone, viz. cadmium, is deposited. But eventually the tension begins to increase up to the value where the deposition of zinc becomes possible, i. e. from 2.6 to 2.8 V, and at the same time the current decreases from 10.5 to 9.5 mA.

The deposit immediately darkens. And immediately too the cathode potential jumps from 0.502 to 0.798 V. Now with a current of 9.5 mA and a tension of 2.8 V the process of electrolytic deposition takes a very long time. Quite differently, however, proceeds the electrolytic deposition of Zn-Cd if such admixtures as dextrin, coffein and cresolsulphonic acid are introduced into the bath.

Influence of Dextrin. If dextrin is introduced into the sulphate bath in a quantity from 0.2 to 7 g per litre, with a current no less than 10.5 mA and a tension no more than 2.6 V, only cadmium is deposited just as in the absence of dextrin, although the quality of the deposit is considerably better. Eventually, the tension begins to increase and the current to decrease, just as in the absence of dextrin. A few seconds later, however, according to the concentration of the dextrin, the tension drops again from 2.8 to 2.6 V instantaneously and the current increases from 9.5 to 10.5 mA. But a new increase in the tension and a new decrease in the current follow soon, and this is repeated again and again. In other words, periodical variations in the current tension on the electrode potential take place spontaneously and simultaneously (Table 1).

Table 1

Periodic Variation of the Current, Tension and Cathode Potential during the Deposition of the Alloy Zn—Cd from Sulphate Baths (in the presence of 3 g of dextrin per litre; area of cathode surface 6 cm²).

Current, mA	Tension on electrodes, V	Cathode potential, V	Notes
1	1.95	0.459	
3	2.25	0.466	A very dense and light coloured deposit
5	2.3	0.470	
8	2.42	0.478	
10	2.5	0.498	
10.5	2.6	—	The tension on the electrodes increased spontaneously from 2.6 to 2.8 V. The current decreased from 10.5 to 9.5 mA. The deposit turned a little darker. After 14 sec. the tension decreased spontaneously to 2.6 V and the current increased to 10.5 mA, and so on.
9.5	2.8	0.788	
10.5	2.6	0.498	
9.5	2.8	0.788	
10.5	2.6	0.498	

Further experiments showed that this periodic oscillation of the current strength, tension and electrode potential depends very much upon the concentration of the admixtures introduced. The results of the study of the influence of the dextrin concentration on the periodic variation in the tension, current strength and cathode potential are given in Fig. 1.

In Fig 1. *a* is variation of cathode potential; *b*, variation of tension on electrodes; *c*, variation of current.

If we change the tension on the electrodes a very little during the periodic deposition of Zn-Cd, the period also changes (i. e. the duration of Zn and Cd deposition). With increasing tension, the period of Zn deposition increases and the period of Cd deposition decreases. Decreasing the tension on the electrodes very little results in an increase in the period of Cd deposition and in a decrease in the period of Zn deposition.

If the alloy Zn-Cd is deposited periodically for 2—3 hours, the fluctuation limits of the tension and current change spontaneously. Thus, for instance in a sulphate bath containing 3 g dextrin per litre in the beginning of electrolysis the tension fluctuates from 2.6 to 2.8 V and the current from 9.8 to 9 mA. At the end of the second hour the tension fluctuates from 2.8 to 3 V and the current from 9 to 8.2 mA. This change in the fluctuation range takes place gradually. With low concentrations of dextrin, 0.3 g per litre, the current, tension and cathode potential cease to change altogether by the end of the first hour.

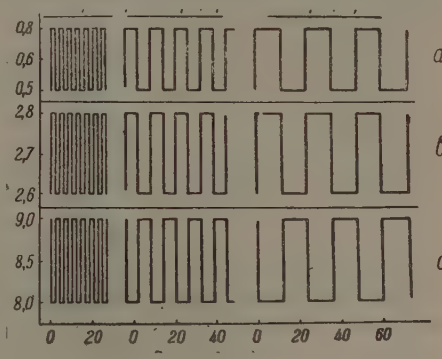

Fig. 1.

With a concentration of 0.5 g per litre and higher periodic deposition continues several hours. If, however, electrolysis is performed on the same bath on the next day, periodic deposition is very weak and soon ceases. The reason is the coagulation of the colloid which can easily be noticed visually.

The fluctuation limits of the current and tension are changed by stirring the bath during the deposition of the alloy; thus, without stirring the tension varies from 2.6 zo 2.8 V and the current from 8 to 9 mA; but if the bath is stirred, the tension varies from 2.9 to 3.1 V and sometimes even more, the current from 28 to 29.5 mA. Furthermore, the periods of Zn and Cd deposition change in length, but this change is irregular.

Influence of Coffein. If coffein (Kahlbaum brand) is introduced into the bath in a quantity from 0.1 to 0.8 g per litre during the process ot depositing Zn-Cd from a sulphate bath, the tension, current and cathode potential vary periodically, as described above.

Stirring and changing the terminal voltage during the process of periodic deposition of Zn-Cd in the presence of coffein influence the deposition periods of these metals in much the same way as in the case with dextrin. In the presence of coffein periodic deposition of the alloy Zn-Cd continues the next day, since coffein does not coagulate. The pH of the solution in the presence of coffein is 2.3. If the concentration of cadmium ions in the solution is increased in the presence of either dextrin or coffein, current and tension change their fluctuation limits (Table 2).

If the current is 150 mA, the periodic deposition of Zn-Cd on the cathode can be observed visually, i. e. one sees the periodic darkening and lightening of the cathode. Darkening (deposition of Zn) always begins in the lower part of the cathode and spreads upwards in the form of a wave in 3 sec. Then lightening follows, and continues also for 3 sec. After the lightening darkening follows again, and so on. The addition of dextrin to the bath increases the fluctuation period. Further increase of the limit of current fluctuation interrupts periodic deposition, since hydrogen is liberated.

Influence of Cresolsulphonic Acid. The presence of cresolsulphonic acid in the bath in a quantity of 10 cm^3 per litre

Table 2

Change of Fluctuation Limits of Current and Tension in Relation to the Concentration of $CdSO_4$ (surface of cathode 6 cm^2)

Concentration, g/l	Fluctuation of current, mA	Fluctuation of tension, V	Fluctuation period in sec.
16	10—10.6	2.6 —2.8	14
32	20.5—21.5	2.84—3.1	15
62	45—46	3.1 —3.35	15
132	150—153	3.8 —3.98	3

also causes periodic variation of the tension, current and cathode potential. Yet, the fluctuation period is very small, 3 sec. under these conditions, and very shortly the periodicity disappears altogether.

A quantitative chemical analysis of the electrolytic precipitates produced by periodic deposition in the presence of dextrin and coffein showed that these precipitates contain only from 20 to 35% Zn. The high cadmium content in the deposit was due to the fact that electrolysis was always begun at low current and low tension, which were quite enough for the deposition of cadmium, but not enough for the deposition of zinc. Thus, at the beginning of electrolysis only cadmium was deposited and only after a current of definite strength and definite tension had been attained did the periodic deposition of both metals begin.

The introduction of peptone into the bath in quantities from 0.2 to 0.4 g per litre does not give periodic deposition. It is true, in the beginning some periodicity may be observed, but it soon disappears. The presence of gelatine in the bath does not make the tension, current and potential vary periodically. The quality of the deposit in the presence of admixtures which do not cause periodic variations in the tension, current and cathode potential (gelatine, peptone) is considerably worse than the quality of the deposit produced with active admixtures (dextrin, coffein, etc.). Therefore, the quality of the deposit which forms during electrolysis appears to be an essential factor in the periodic deposition of the alloy. Besides that such admixtures as peptone and gelatine under the bath condition coagulate considerably quicker than dextrin. For this reason these admixtures do not cause periodic deposition.

It is the Cd ions which are known to become discharged if a solution containing $ZnSO_4$ and $CdSO_4$ becomes electrolyzed higher than the decomposition voltage of $CdSO_4$ and lower than that of $ZnSO_4$.

As a result of the discharging of Cd cations, its concentration decreases greatly in the first moment after the current is switched on. However, the discharged ions are compensated for by way of diffusion, mobility and convexion. If compensation is insufficient, the concentration of Cd ions decreases during the electrolysis and with that the tension increases, and the current decreases. In our case the increase in voltage during the deposition of Cd is only up to the magnitude, at which Zn begins to deposit. Zinc deposits until the concentration of Cd ions around the cathode layer due to diffusion attains a certain value, with this value obtained the deposition

of Zn ceases, since there are enough Cd ions to be discharged at this current strength.

Since the decomposition voltage of cadmium sulphate is less than the decomposition voltage of zinc sulphate and the energy given to the electrodes by the accumulators stays constant, a decrease in the decomposition voltage of $CdSO_4$, the resistance of the circuit remaining constant, results in the current increasing and the cadmium depositing. Cadmium continues depositing until, as a result of the concentration of Cd ions around the cathode layer having decreased, the voltage again attains the value corresponding to the decomposition of zinc sulphate. When this voltage value is reached, zinc again begins to deposit and so on.

As we have already mentioned, this periodic deposition of the alloy is observed only in the presence of certain admixtures and the fluctuation period depends upon their concentration. Consequently, if there are no admixtures, the decrease in the concentration of Cd around the cathode layer is compensated for by the diffusion of Cd ions from the surrounding space. But if there are admixtures present, the Cd ions, being of low concentration, evidently become exhausted, due to possible chemical, adsorptive or electrostatic interactions between the ions and the admixtures. As a result of this the transportation of adsorptive complexes containing cadmium to the cathode is slowed down. Due to this zinc deposits, and we get the periodic deposition of the alloy Zn-Cd described in this publication.

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PHYSICAL CHEMISTRY

NEW HEAT-RESISTING CHROME-ALUMINIUM STEELS OF HIGH ELECTRICAL RESISTIVITY. I

By I. I. KORNILOV

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Physical-chemical analysis applied to the study of the relationship between changes in the chemical composition of a system and its properties, affords the possibility of finding new compositions for metallic alloys with the most advantageous physical-chemical and mechanical properties. In this respect the principle of «composition—property» equilibrium diagram developed by N. S. Kurnakov (1) and collaborators favourably compares as a scientific method of investigating metallic alloys with the purely fortuitious, empirical searching for new alloys which prevails in practice.

One of the applications of the theory of physical-chemical analysis to the development of new alloys was a work on the investigation of the diagram of state of the ternary system iron-chromium-aluminium (2) carried out under the guidance of the author in this Institute.

Is is known from the theory of physical-chemical analysis that solid solutions of metallic alloys are of high specific electrical resistance, and owing to their homogeneity are also most resistant to high temperatures. From the literary data on the binary systems: iron-chromium, iron-aluminium and chromium-aluminium, it was to be expected that a wide range of solid solutions of chromium and aluminium with the specific physical properties mentioned above should form in α-iron. By studying the diagram of state of iron-chrome-aluminium alloys (see next article), the author succeeded in producing steels which proved to be superior to all the special alloys heretofore available in respect of electrical and heat resistance. This will be obvious from the data of the table where the high-resistivity alloys available are compared with the new chrome-aluminium steels on the basis of their specific properties.

Of the high-resistivity alloys given in the table, the alloys fechral and chromal cannot be considered suitable for industrial application as yet, since the first of them, fechral, is not sufficiently heat-resisting, while chromal is not worked mechanically without considerable difficulty.

From the table it follows that the new steels developed by us show, on the one hand, high electrical resistivity and low temperature coefficient of electrical resistivity; while, on the other hand, on account of their good heat-resistance they may be applied up to high temperature maxima.

The high specific resistance of the new steels is to be explained by the circumstance that these alloys are homogeneous and by nature more concentrated solid solutions of chromium and aluminium in α-iron, with greatly reduced

Alloy	Metallic basis	Specific electric resistance, ohm. mm²/m	Temperature coefficient of resistance $\alpha = 20-100°$	Upper range of resistible t, °C
Existing alloys				
Constantan	Copper (50—60%)	0.48—0.50	0.00003	350—340
Manganin	» (84—86%)	0.30—0.50	0.0003	250—300
Nickelin	Copper and nickel (65% Cu + 30—35% Ni)	0.35—0.40	0.0002	350
Nichrome I	Nickel (78—80 %)	1.05—0.18	0.0001	1100—1150
Nichrome II (with iron)	» (60—65%)	1.10—1.15	0.00015	900—1000
Fechral	Iron (82—85%)	1.10—1.20	0.00009	700— 800
Chromal«Megapyr»	» (65%)	1.20—1.40	0.00004	1200—1250
New alloys				
P	Iron (85—90%)	1.40—1.60	0.00004	800— 900
№ 1	» (75—78%)	1.40—1.60	0.00003	1000—1100
№ 2	» (65—69%)	1.50—1.70	0.000025	1200—1250
№ 3	» (50—55%)	1.70—1.90	0.000020	1350—1400

content of those admixtures which are responsible if present in higher proportion for the appearance of an excess phase. The presence of an excess phase on the boundaries of the grains which occurs in fechral and chromal makes them more difficult to work and reduces their heat-resistance.

The considerable increase in the heat-resistance of the new steels may be explained as follows: homogeneous alloys of iron-chromium-aluminium become covered with a thin film of oxide on heating to high temperatures, and this preserves the alloy from further oxidation. This oxide film which consists of the sum of the oxides Al_2O_3, Fe_2O_3 and Cr_2O_3 is also obviously a homogeneous solid solution of these oxides, since, according to published information, the binary systems Al_2O_3—Fe_2O_3, Al_2O_3—Cr_2O_3 and Fe_2O_3—Cr_2O_3 form continuous solid solutions between themselves. Provided that there are no foreign admixtures in the alloy and that the transformation in the solid state takes place, such a uniform film is preserved without destruction for long periods of time and is thus a reliable covering, protecting the surface of the metal from further oxidation. The presence of foreign admixtures (such as non-metallic inclusions in the form of oxides or sulphides) causes breaks in the uniform oxide film at points around which further oxidation of the metal takes place. One of the basic reasons for the reduction in the heat-resistance of heterogeneous alloys, and in particular fechral and chromal, are, as we consider, physical-chemical transformations which take place in these alloys at high temperatures. These transformations are mainly connected with transition of the excess phase to a solid solution on heating. The actual process of dissolution of this phase at high temperatures is obviously associated with destruction of the crystalline lattice of the disappearing phase and the appearance of chemical activity of the atoms at points of transition of the excess phase into solid solution. This circumstance will doubtless intensify the oxidation of the alloy by destruction of the continuous uniform oxide film.

The repeated heatings and coolings which alloys of this type undergo in their technical applications and which cause the successive appearance

and disappearance of the excess phase at high temperatures in the solid state, still further accelerate the process of destruction of the uniform oxide layer and thus reduce the heat-resistance of the alloys. In accordance with the above considerations we will consider it as established that the new chrome-aluminium steels, which are more homogeneous than the existing chromal and fechral, are also more heat-resisting and able to withstand prolonged heating to temperatures of 1200—1300° without appreciable destruction.

The division of our steels into four groups according to their composition characterizes different regions in which they may be applied as electrically resistant alloys. From the results of preliminary tests of the new materials the following applications have been indicated for them: alloy P will be a comparatively cheap material for rheostats and electrical heating apparatus to replace nichrome, constantan and other alloys in which there is a shortage in this country. Alloy No. 1 will replace nichrome materials in laboratory and industrial types of electric furnaces with a temperature limit of 1000—1100° and will also be used for various domestic electric appliances. Owing to its high electrical resistivity, heat-resistance and plasticity, alloy No. 2 may be applied as heating element material for various types of electric furnace with working temperatures of up to 1200—1250° and in particular may be used to replace expensive platinum in laboratory types of electric furnace. Finally, alloy No. 3 is obtained in the form of ribbons and wires by hot-working and may be used for heating elements to work at very high temperatures of up to 1350—1400°, at which it still has quite a long life. From this viewpoint alloy No. 3 may be used to replace imported silit «globar» which is used to obtain furnace temperatures of 1300—1350°.

In addition to the basic application of these new steels as materials for electric heating elements and rheostats, it is to be expected that applications will also be found for them as heat-resisting steels for various products which have to work under conditions of high temperature, steels which are stable to various chemical reagents (in particular, to sulphur compounds and organic acids) and so on. Obviously, the problem of finding extensive applications of the principal advantageous properties of the new steels should be set before a number of scientific institutes and factory laboratories for their joint solution, so that these steels which consist of native materials (iron, chromium, aluminium) should find the widest possible applications and replace those which are expensive or fall short.

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PHYSICAL CHEMISTRY

INVESTIGATION OF THE EQUILIBRIUM DIAGRAM OF THE TERNARY SYSTEM IRON-CHROME-ALUMINIUM. II

By I. I. KORNILOV, V. S. MIKHEJEV and O. K. KONENKO-GRACHOVA

(Communicated by N. S. Kurnakov, Member of the Academy, 16. V. 1939)

Alloys of the system iron-chrome-aluminium present considerable interest on account of their ability with definite proportions of the respective components to acquire high heat-resistance and high electrical resistivity. These two properties, resulting from the nature of the chemical interaction between the three components, are an essential prerequisite of the practical application of these alloys as high-heat materials in electric furnaces and other electrical resistance apparatus.

From the literature on the subject it is well known that the binary system iron-chrome is characterized by the availability of a continuous solid solution and by the formation out of this solid solution of the intermetallic compound FeCr([1], [2]). On the other hand, the system iron-aluminium shows that aluminium is capable of dissolving in iron in the solid state up to 33 %([3],[4]), while the interaction of aluminium and chrome is, according to the latest information, characterized by the fact that chrome is capable of giving solid solutions with aluminium to the amount of 17% ([5]).

The diagrams of state of the binary systems iron-chrome, iron-aluminium and chrome-aluminium are plotted along the sides of an equilateral triangle (Fig. 1). Literary data as to the diagram of state for the system iron-chrome-aluminium are lacking.

We have carried out investigations of the iron side of the diagram of state for the system iron-chrome-aluminium within the limits: for Al up to 40%, and for Cr up to 100%. The choice of pure metals as well as convenient procedures of preparation of uncontaminated alloys are of the utmost importance in the study of chemical interaction of elements and in finding out the correlation between the chemical composition of the system and its properties. As our initial charge we made use of Armco-iron with 0.02% carbon and occasionally of electrolytic iron. However, the addition of chrome and aluminium into this charge involved considerable difficulty. We succeeded, however, in obviating this having worked out a special alumino-thermal procedure for obtaining Cr-Al alloys ([5]) within the limits of up to 30% Al, and these intermediate alloys were introduced into the pure iron charge for securing the proper composition of the required ternary alloys. The preparation of the iron-chrome-aluminium alloys on the aluminium side was likewise effected by means of obtaining preliminary iron-aluminium alloys (about 50%).

The equilibrium diagram of the system in question was studied by means of the following methods of physical-chemical analysis: thermal analysis, microstructure, hardness and conductivity.

According to the equilibrium diagram for the binary systems involved in the ternary system under consideration we might expect the formation of a ternary solid solution, viz. one of chrome and aluminium in α-iron. The results of thermal analysis represented by the cooling curves from a Kurnakov pyrometer show that in the course of crystallization, in the iron corner of the ternary system Fe-Cr-Al precipitation of a ternary solid solution occurs within a wide range of chrome and aluminium content. By means of microscopic examination as well as hardness and conductivity measurements, we succeeded to determine the limits of the field occupied by the ternary solid solution as dependent on aluminium and chrome content and temperature.

The results of the investigation of iron-chrome-aluminium alloys by the method of physical-chemical analyses are summed up in the diagram of state

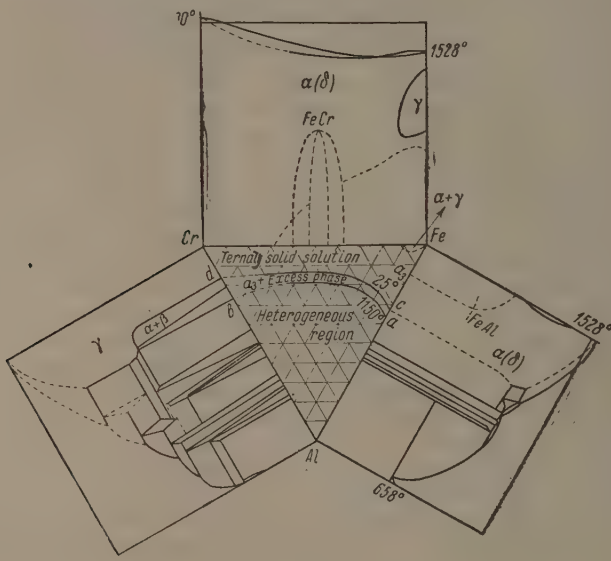

Fig. 1.

for the ternary system investigated, which is represented in Fig. 1. In the diagram are to be found data on the limit of the field taken up by the ternary solid solution α_3 for two states. The first is the case of alloys quenched from 1150° and the second—that for alloys annealed at this temperature with subsequent slow cooling.

For quenched alloys the equilibrium diagram is characterized by that the field of the ternary solid solution at the temperature of quenching is confined by curve *ab* which curve begins on the side of the double system Fe-Al, and runs inside the triangle with its convexity toward the Fe-Cr side. Such a direction of the curve testifies to a decrease in solubility of aluminium in iron in the solid state with chrome additions. Alloys annealed at the above temperature and slowly cooled down to room temperature display a more complex picture, which is due not only to a decrease in the joint solubility of Al and Cr with lowering of temperature, but also to transformations in the solid state within the region of the intermetallic compounds: FeCr and Fe_3Al.

The curve *cd* of the joint solubility of Al and Cr in iron in the annealed condition shows a picture nearly analogous to that of the curve for the joint solubility of alloys quenched from 1150°, with the only difference that the range of this solubility is found to decline appreciably. The two photomicrographs given in Fig. 2 and 3 can serve to illustrate such a decrease.

The first photomicrograph (Fig. 2) corresponds to the homogeneous structure of an alloy 20% Cr and 19% Al quenched from 1150°, while the second one (Fig. 3) corresponds to the same composition of the alloy, but in an annealed state. As seen from the microstructures, precipitation of the excess phase in the form of white inclusions along the grain boundaries is observed in the case of slow cooled alloy, instead of the homogeneous structure, in the quenched one.

The region of the ternary solid solution in the annealed condition becomes appreciably reduced by the transformations occurring in the ternary system, which are connected with the formation in solid state of the double chemical compounds FeCr and Fe_3Al. A more detailed study of the phases precipitated

Fig. 2.

Fig. 3.

in the solid state is now in progress. The results of these investigations will be discussed by the authors in their forthcoming article; therefore the respective data are not given in diagram.

In the diagram (Fig. 1) is to be found the region of the existence in the ternary system of two phases $\alpha+\gamma$ for isotherm 1150°, which can be quite definitely established by the method of microstructure and hardness.

From the theory of physical-chemical analysis advanced by Kurnakov (7) it follows that in solid solutions electrical resistivity is liable to rise in proportion with the growth of concentration of the substance dissolved in the solid state. This statement makes the leading principle in our work; indeed, we took it for granted that the more concentrated the solid solutions of the alloys, the greater the electrical resistivity we were likely to expect.

The above theoretical assumptions have been fully confirmed in the course of investigation of the equilibrium diagrams. It was shown, moreover, that in the region of ternary solid solutions of the system iron-chrome-aluminium we, actually, deal with alloys showing high electrical resistivity. The latter is besides liable to rise with increase of the concentration of chrome and aluminium in the solid solution.

We succeeded in finding such alloy compositions which display a higher electrical resistivity than that in nichrome and even better than the resisti-

vity shown by such modern alloys as chromal and fechral. While industrial fechral (13% Cr, 3—4% Al) has $\rho = 1.1—1.2$ Ω per mm²/m, and chromal (30% Cr. 3—4% Al)—1.20—1.40 Ω, our alloys, while having a higher content of chrome and aluminium in the solid solution, show an electrical resistivity running as high as 1.5 to 2.0 Ω; certain of the most concentrated solid solutions show even an electrical resistivity of 2.5 to 3.0 Ω per mm²/m. The electrical resistivity is plotted against composition in the diagram «Composition—specific electric resistance». This diagram for the alloys of the ternary system Fe-Cr-Al and, moreover, a special investigation of the heat-resistance of some of the alloys in this system, have provided a scientific basis for working out new compositions of heat-resisting alloys which might serve as substitutes for nichrome, platinum and other materials used in the manufacture of electric heating elements with different temperature ranges of application (see the preceding article).

Conclusions. 1) As a result of an investigation of the alloys of the ternary system iron-chrome-aluminium a region of ternary solid solutions α_3 has been found, existing in alloys quenched from 1150° and annealed at the same temperature with subsequent slow cooling. 2) The transformation making a change in the joint solubility of chrome and aluminium in α-iron has been determined. 3) On the basis of the diagram «Composition—property» new alloys have been developed showing high heat and electrical resistance which may be applied in national economy on an industrial scale as electric heating materials and heat-resisting alloys.

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PHYSICAL CHEMISTRY

TECHNOLOGY OF NEW HEAT-RESISTING CHROME-ALUMINIUM STEELS OF HIGH ELECTRICAL RESISTIVITY. III

By I. I. KORNILOV and V. S. MIKHEJEV

(Communicated by N. S. Kurnakov, Member of the Academy, 16. V. 1939)

From investigation of the diagram of state of the system iron-chromium-aluminium (see previous article) the compositions of alloys highly resistant to heat and electric current were established. The results of this work served as a scientific foundation for development of the technology of the new heat and current-resisting chrome-aluminium steels, with improved physical-chemical properties compared to available types of alloys, the fechral and chromal.

The problem in question seemed to us the more urgent in that high-resistivity alloys of the type of fechral and chromal as they are produced at present, show low heat-resistance and poor mechanical working properties, owing to their considerable content of admixtures of carbon and silicon, which cause the appearance of an excess phase in the alloys when present in more than certain concentrations. Reduction of the aluminium content (to 2—4%) in the two alloys still further reduces their heat-resisting power. This accounts for the fact that continual efforts during 5—6 years of establishing the production of chromal and fechral in this country have not been crowned with expected results. In addition, the problem of replacing the short-running nichrome, the expensive platinum and other imported materials (silit) which are at present employed as elements in electric furnaces of laboratory and factory types, urgently necessitates the mastery of the production of the new alloys which consist of native materials and have better physical and chemical properties than even nichrome, fechral and chromal.

Proceeding from experimental data on the diagram of state of the system iron-chromium-aluminium and from the new technological scheme of production of chrome-aluminium steels, we carried out 25 experimental smeltings of the new and high temperature resisting steels at the Electrostal works, in a high-frequency furnace of 50 kg capacity, and proceeded to work the alloys until the finished product was obtained in the form of wires, ribbons, strips and sheets. The compositions of the steels prepared follow from their optimum physical-chemical properties, the chromium content varying from 10 to 50% and the aluminium content from 0 to 20%.

The main problem in the new technology of chrome-aluminium steels was that of effecting a considerable change in the chemical composition of the steels obtained, the reduction of harmful admixtures of carbon, silicon,

sulphur and others, and of radically improving the introduction of aluminium into the steel. For this purpose we developed an alumino-thermic method of obtaining carbonless chromium-aluminium alloys and steels [1]. This method which is one of the simplest chemical-metallurgical processes of obtaining alloys makes it possible to obtain rapidly, without a furnace, the binary and ternary alloys required in the production of the new high-quality chrome-aluminium steels.

In addition to producing chrome-aluminium and iron-chrome-aluminium alloys without a furnace, we obtained iron-chromium-aluminium alloys by a combination of the process of melting the iron in a crucible with that of alumino-thermic reduction of chromium oxide or chromium-ore concentrates with excessive aluminium. In all these methods of preparing the new high-quality chrome-aluminium alloy steels we have so far only considered the method of obtaining the chrome-aluminium alloy, as the most readily available and the simplest process. In our subsequent work we will attempt other methods of preparing these steels.

Preliminary production of carbonless alloys with varying aluminium content (from 5 to 30%) carried out at the Zestafon works made it possible to prepare chrome-aluminium steels of any desired composition, with very much reduced content of carbon, silicon and manganese, which considerably improved the introduction of aluminium into the steel.

In the existing methods of smelting aluminium steels, the aluminium is introduced at the end of the process when, owing to its low specific weight, it does not mix well with the steel and is intensely oxidised, so that the quantity of oxides of aluminium in the steel is greatly increased and uniform distribution of the aluminium is not attained. By the method of introducing the aluminium in the form of a chrome-aluminium alloy during the smelting process, good mixing of the iron and aluminium is attained, there is a sharp reduction in the loss of aluminium by burning (from 25—30% with the existing methods to 0% with the new method) and the reduction of the aluminium oxide content in the steel; there also results a more uniform distribution of the aluminium throughout the entire mass of molten steel.

During the process of smelting of new chrome-aluminium steels we used synthetic slag, consisting of three basic oxides, CaO, MgO and Al_2O_3. With a certain proportion of the constituents, this slag has a low melting temperature (1345°C) and is a good protective cover to preserve the surface of the metal from oxidation. Owing to the constant movement of the metal in the crucible in high-frequency furnace, the application of this basic low melting-point slag created favourable conditions for the interaction of the molten slag with non-metallic inclusions in the metal, and their gradual removal

Steel	Constituents, %					
	Fe	C	Si	Mn	S	P
New [chrome-aluminium steels	85—86	0.03—0.04	0.20—0.30	0.1	0.003	0.008
	75	0.02—0.03	0.20—0.30	0.1	0.004	0.008
(Cu 10—50%, Al 0—20%) .	65—68	0.02—0.03	0.20—0.30	0.1	0.006	0.010
	55—58	0.02—0.03	0.20—0.30	0.1	0.006	0.009
Fechral (Cr 12—14%, Al 3—4%)	83—85	0.15—0.25	0.5 —1.5	0.5—1.0	0.02	0.03
Chromal (Cr 27—30%, Al 2.5—4%)	66—68	0.15—0.20	0.5 —1.2	0.5—0.8	0.02	0.03

from it by dissolution in the slag, since they occur in the molten metal in the form of mechanical admixtures and in the slag in the form of a solution. The method of smelting described above demonstrated the possibility of obtaining high-quality chrome-aluminium steels containing very small quantities of admixtures.

In the table we give specimen compositions of the new heat- and current-resisting steels and a comparison between the composiion of them and commercial chromal and fechral.

As will be seen from the table, in all the compositions of the steels which we prepared the carbon content is 8—10 times less and that of silicon 3—4 times less than in chromal and fechral, whilst the manganese content is reduced to 0.1% and those of sulphur and phosphorus to a few thousandths of one per cent instead of 0.02—0.03% in fechral and chromal.

These steels so low in admixtures responsible for the appearance of an excessive phase, naturally, give either quite homogeneous solid solutions or with an inconsiderable separation of the phase in the region of existence of the

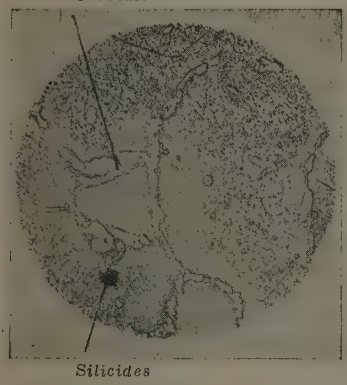

Fig. 1.

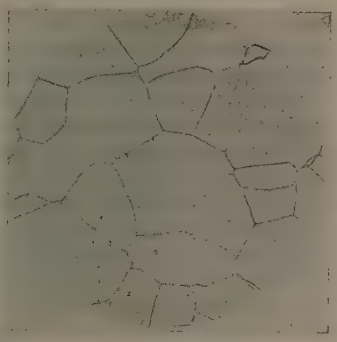

Fig. 2.

inter-metallic compound FeCr. Such a sharp difference in the microstructure—on the one hand, a coarse mechanical mixture of carbides and silicides with a ternary solid solution in the structure of commercial chromal (Fig. 1) and, on the other, the uniform polyhedral structure of the solid solution in the majority of the new steels (Fig. 2)—explained the bad working properties of chromal and predicted good working properties for the new chrome-aluminium steels, even with increased content of chromium and aluminium.

In carrying out the experimental smelting we succeeded in forging steels with a Cr content from 10 to 50% and Al content from 0 to 10%. Alloys containing more than 10% aluminium could not be forged, even though they were uniform solid solutions. Here a factor were probably the stresses, which arise in the lattice of α-iron from simultaneous solution in the solid state of considerable quantities of chromium and aluminium with different atomic radii. Bad thermal conductivity and a comparatively high coefficient of thermal expansion of steel had undoubtedly a part in this, too. During heating and cooling of the ingots under industrial conditions these two factors cause the appearance of internal stresses, as a result of which cracks are formed in the alloys, and these are the main cause of destruction of the ingots on forging.

Further working of the forged ingots showed that iron-chrome-aluminium alloys with a content of Cr up to 45% and Al up to 9—10% may be rolled

in a normal manner in the hot state to 8 and 5 mm diameter wires, to ribbons, strips and sheets, which can be used directly as heat- and current-resisting materials in technical applications. While working these steels in the cold state it was found that wires of any desired section could be drawn and strips could be rolled from alloys considerably higher in aluminium than is possible in the case of chromal, and with varying chromium content. The cold-rolling of ribbon is possible in many cases with Cr content of up to 30—35%. Both forms of cold-working (wire-drawing and rolling of ribbon) afforded the possibility of producing standard size materials, which could then be used as electric heating elements or for other applications of heat-resisting materials.

A characteristic feature in working the new heat- and current-resisting steels is that the alloy is relatively brittle at room temperature, but becomes plastic when heated to 200—400° C and can then undergo any sort of deformation. From this viewpoint the properties mentioned may be used to obtain standard size materials from brittle alloys in the hot state, which would exhibit a very high heat-resistance and a long life at high temperatures.

Conclusions. 1) On the basis of investigation of the diagram of state of iron-chromium-aluminium there are developed new compositions for heat-resistant chrome-aluminium steels of high electrical resistivity.

2) A new technology is developed for these steels with the application of a carbonless alloy and synthetic slag.

3) It is shown that homogeneous chrome-aluminium steels with very small contents of harmful admixtures of carbon, silicon and sulphur have properties which make their mechanical treatment much easier and exhibit a high resistance to heat and a high electrical resistivity.

4) By smelting and treating the new steels on a larger scale, new industrial brands of heat-resistant and high electrical resistivity steels were developed.

5) These new brands of industrial alloys may serve as substitutes for nichrome and platinum as materials for electrical heating elements, and may provide substitutes for heat-resistivity steels.

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PHYSICAL CHEMISTRY

A METHOD OF STUDYING THE CAPACITY OF ELECTRODES IN DILUTE SOLUTIONS

By M. A. PROSKURNIN and M. A. VORSINA

(Communicated by A. N. Frumkin, Member of the Academy, 21. VII. 1939)

By applying the method of studying the capacity of metallic electrodes, various problems on the structure of the double electric layer can be solved. An interesting problem is the study of the degree of diffuseness of the double layer. At the present time calculations after Stern and Gouy can be checked quantitatively and at the same time directly only on the basis of data on the capacity of the electrode. Of course, in view of the fact that the diffuse structure of the ionic layer becomes noticeable only at low concentrations of the electrolyte, it is necessary in order to check in this way to turn to a study of weak solutions.

When the electrode potential is far from the charge's zero point, the electric forces which attract the ions onto the surface of the metal are great, and the degree of diffuseness of the double layer is small. On the contrary, at the maximum of the electrocapillary curve the diffuseness of the double layer increases and, consequently, the capacity should be at its minimum value. Thus, the method of capacity measuring puts into our hands a means of determining the position of the charge's zero points in a way independent of other methods. It is important to note that this method should be especially valuable for solid metals, since no other reliable methods are available here.

It may be considered that of all the methods of capacity measuring, the best one for our purposes is the electric method which consists in measuring the variable polarization component when alternating current is passed through the electrode surface in the solution. This kind of measurement was performed up till now at higher concentrations. One of the variants of such a method is described in the work of Borissova and Proskurnin ([1]).

For liquid metals the method of calculating the capacity values from the eletrocapillary curves is applicable in principle, but when dilute solutions are used the accuracy of the measurements falls, because the mobility of the mercury meniscus in the capillary tube goes down. Up till now it has been possible to reach 0.01 n solutions in this manner, but the measurement was not accurate enough to calculate capacities. Philpot ([2]), who directly determined the charge of falling mercury drops, was successful in reaching a dilution of the order of 0.001 n and comparing the data thus obtained with Stern's theory. However, these measurements are also not accurate enough.

In the electric method accepted by the authors in working with very dilute solutions there appear specific difficulties, connected mainly with the low electroconductivity of the solutions.

The polarization component variable $p_{\sim}$ consists of two terms, one of which depends upon the capacity of the double layer, and the other on the ohmic resistance:

$$p_{\sim} = \sqrt{\frac{i^2}{\omega^2 C^2} + r^2 i^2} \qquad (1)$$

where ω is the cyclic current frequency; C, the capacity in farads; r, the resistance of the solution between the two electrodes; i, the current strength. The value ri which determines the «ohmic correction» increases greatly when the solution is diluted and may be somewhat decreased by moving the auxiliary electrode nearer to the one being measured. A decrease in the frequency of alternating current results in the capacity resistance increasing in comparison with the ohmic resistance of the solution.

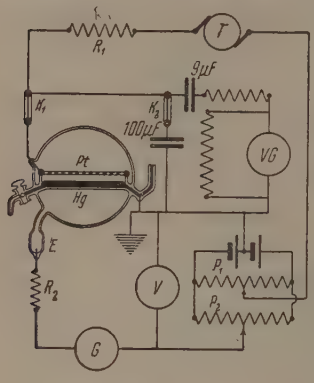

Fig. 1.

On the basis of these considerations we used one-period alternating current and had the possibility of reaching a 0.001 n concentration for salt solutions and 0.0001 n for hydrochloric acid. In order to study even more dilute solutions, it is necessary to use current of even longer period, besides purifying the water, used in preparing the solution, more thoroughly.

In the work referred to above Proskurnin and Borissova applied the «parallel feeding diagram» which is well-known in electrotechnics. They diverted the direct and alternating components of the polarizing current from generators joined in parallel, using separating and blocking condensers and throttles.

Since the blocking apparatus for one-period current are very cumbersome, we used the series feeding system represented in Fig. 1 in this work. The generator Γ is a small alternator, whose rotor does 1 revolution per second. Its rotation velocity is stabilized by means of a synchronic motor. The one-period alternating current passes through a limiting resistance and through the switch into an apparatus, in which there are two electrodes: the auxiliary one of platinum gauze *(Pt)* and the one to be measured of mercury in a glass dish *(Hg)*. Then it goes through a battery of accumulators, a potentiometer P_1 and then back to the generator Γ.

The potentiometer P_1 makes it possible to set a constant polarization on the mercury. The potentiometer P_2 is included in the circuit of the compensation apparatus in order to measure the potential (φ) of the mercury electrode. E is a calomel electrode; G, a zero instrument; R_2, a resistance ($10^5\Omega$) which keeps the alternating polarization current from branching.

If switch K_1 is turned off and K_2 turned on, it is possible to direct the alternating current through the capacity standard (100 μF) instead of the mercury electrode.

A short-period galvanometer VG furnished with a high series resistance serves as a millivoltmeter for the alternating current, and the value of alternating polarization is measured by means of it. The locking condenser 9 μF does not let the direct component of the polarizing current through the galvanometer VG.

Comparing the polarization values $p'_{\sim}$ and $p''_{\sim}$ when the switches K_1 and K_2 are turned on respectively, we get:

$$\frac{p'_{\sim}}{p''_{\sim}} = \frac{\sqrt{\frac{i_1^2}{\omega^2 C^2} + r^2 i_1^2}}{\frac{i_2}{\omega \cdot 100\ \mu F}}$$

where i_1 and i_2 are the current strengths when the switches K_1 and K_2 are turned on.

If the switching resistance R_1 is high, it can be taken that $i_1 = i_2$ and then i can be cancelled respectively in the formula. Thus, it is not necessary to know the magnitude of the alternating current. In some cases, namely in the region of minimum capacity, it was sometimes necessary to take into account the change in current and to introduce the corresponding small correction in calculating the capacity.

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PHYSICAL CHEMISTRY

CAPACITY OF THE DOUBLE LAYER OF THE MERCURY ELECTRODE IN DILUTE SOLUTIONS OF HYDROCHLORIC ACID AND OF POTASSIUM CHLORIDE

By M. A. VORSINA and A. N. FRUMKIN, Member of the Academy

The method described in the last paper was used to plot the capacity curves of a mercury electrode in dilute solutions of hydrochloric acid and of potassium chloride. The mercury used was twice distilled. The potassium chloride was from Kahlbaum, the brand «for analysis». It was purified from organic substances by heating it red hot. The water used in preparing the solution was twice distilled and had a conductivity of from 0.7×10^{-6} to 0.9×10^{-6} mho. The hydrochloric acid solutions were prepared from freshly produced hydrogen chloride. The electrolytic cell for measuring the polarization capacity on mercury was made of Jena glass, about 400 cm^3 in volume. The main parts of the cell are as follows: a dish filled with mercury, in which the surface area of the mercury is 36.3 cm^2; there is a platinized platinum gauze over the surface of the mercury which serves as auxiliary electrode; a calomel electrode prepared with the same solution was used for comparison. The potential of the calomel electrode when the concentration of the hydrochloric acid was 10^{-4} n, was unstable, and therefore it was necessary to compare it with a normal calomel electrode and make respective corrections in measuring the capacity curves. The electrolytic cell was joined to the hydrogen apparatus by means of a ground glass joint. Before the experiment electrolytic hydrogen was passed from a spiral tube submerged in liquid air through all the parts of the cell for 3—4 hours. None of the ground glass joints nor taps were greased, but just wetted with the same solution.

Since there is a platinized platinum screen in the cell serving as auxiliary electrode, when it is saturated with hydrogen, hydrolytic adsorption of the salts from the solution is possible, liberating acid, which may affect the conductivity of dilute potassium chloride solutions. Our measurements of the conductivity of a $10^{-3}n$ potassium chloride solution did not show any noticeable difference before and after the experiment, however when the concentration was 10^{-4} n a difference could be observed.

The distance between the mercury and the auxiliary electrodes could be regulated by varying the level of the mercury. The resistance of the solution which filled up the space between the mercury and the platinum screen was measured while plotting the capacity curve, whereby use was made of a current of higher frequency. We plotted the capacity curves for the following solutions: 1 n KCl, 10^{-1} n KCl, 10^{-2} n KCl, 10^{-3} n KCl, 10^{-3} n HCl, 10^{-4} n HCl. The curves given in this paper are the average of a large number of experiments. As mentioned in the last paper, the ohmic corrections were

taken into account in calculating the capacities of solutions of low conductivity. Fig. 1 shows the experimental capacity curves of the mercury electrodes where the capacity values are plotted along the ordinate axis, and the potential values of mercury φ referred to a normal calomel electrode—along the abscissa axis. Measurements with alternating current, of course, immediately give the value of differential capacity $\left(\frac{\partial \varepsilon}{\partial \varphi}\right)$, where ε is the charge per unit surface. On the capacity curve of the normal potassium chloride solution there is a small maximum which has already been described before in a paper by Borissova and Proskurnin. The curve of the decinormal solution consists of two almost horizontal branches which correspond to a double layer formed of anions and cations respectively, and a connective branch with intermediate capacity values. At high positive or negative surface charges the capacity value increases due to the deformation of ions. This curve does not give any indication of a diffuse structure. However, a minimum although an indistinct one as yet, appears already on the curve of the 10^{-2} n solution of potassium chloride, near the zero charge point, and in the 10^{-3} and 10^{-4} n solutions this minimum which was observed at $\varphi = -0.53$, in excellent conformity with the determination of the zero charge point according to electrocapillary data, is very distinctly expressed.

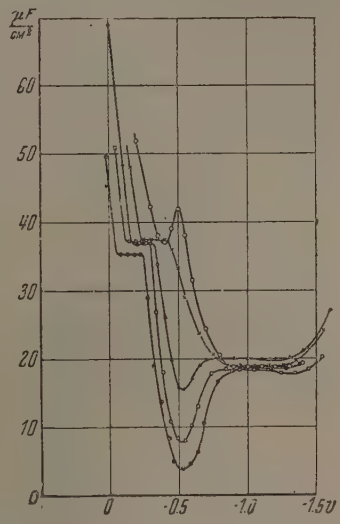

Fig. 1. Capacity of mercury electrode after experimental data: ○○○—norm. KCl; ×××—0.1 n KCl; ▲▲▲—0.01 n KCl; □□□—0.001 n KCl; ●●●—0.0001 n KCl.

The minimal capacity value on the curve of the 10^{-2} n potassium chloride solution equals 16 μF, on the curve of 10^{-3} n KCl it equals 7.9 μF, and on the capacity curve of the 10^{-4} n hydrochloric acid solution this value equals 3.9 μF. From Gouy and Stern's theory it follows that the double layer has the most diffuse structure near the zero charge point. When the absolute value of the charge increases, ions are attracted to the surface and the double layer changes in structure from diffuse to non-diffuse. As a result of this the average thickness of the double layer should be a maximum, and the capacity—a minimum at the zero charge point. It was interesting to compare the results of our measurements with the values of $\frac{\partial \varepsilon}{\partial \varphi}$ calculated according to Stern's theory.

Taking for granted that ions are not adsorbed specifically, neglecting the influence of occupying the surface on the adsorption and assuming the thickness of Helmholtz's layer to equal the diameter of a molecule of water, we can write the equation of Stern's theory in the following form:

$$\varepsilon = K(\varphi - \psi_1) = 2cdF \sin \text{hyp} \frac{\psi_1 F}{RT} + 4c\lambda F \sin \text{hyp} \frac{\psi_1 F}{2RT} \qquad (1)$$

where ψ_1 is the potential value at a distance of one ionic radius from the surface of the mercury; d, the diameter of a molecule of water (3.1×10^{-8} cm); λ, the thickness of the ionic atmosphere for a uni-univalent electrolyte at a given concentration according to Gouy-Debye; K, the capacity of the non-diffuse layer; c, the concentration expressed in gram-equiv. per cm³.

The first and the second term on the right side of equation (1) express, as we know, the charge of the non-diffuse and of the diffuse part of the double layer, respectively. However, equation (1) cannot be used for calculating $\frac{\partial \varepsilon}{\partial \varphi}$ and comparing the value thus obtained with experimental data in the whole interval of measurable potentials, since it assumes that the value K is constant for all values of φ; actually, however, the value of K is doubtless different for a positively and negatively charged surface. Therefore this equation was modified by introducing two capacity values of Helmholtz's layer K_1 and K_2 which are characteristic of a double layer formed of anions and cations, respectively. Under these conditions K of equation (1) should be considered a variable depending upon the concentration of anions and cations in Helmholtz's layer. Since these concentrations are proportional respectively to $\exp \frac{\psi_1 F}{RT}$ and $\exp\left(-\frac{\psi_1 F}{RT}\right)$, the most simple way is to take the value K equal to:

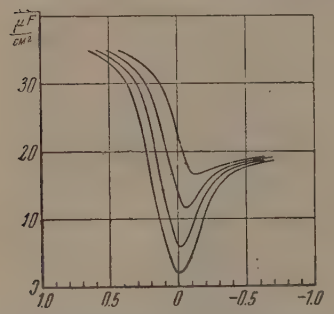

Fig. 2. Capacity of mercury electrode calculated after Stern's theory for a 0.1; 0.01; 0.001 and 0.0001 n solution (from top to bottom).

$$K = \frac{K_1 \exp \frac{\psi_1 F}{RT} + K_2 \exp\left(-\frac{\psi_1 F}{RT}\right)}{\exp \frac{\psi_1 F}{RT} + \exp\left(-\frac{\psi_1 F}{RT}\right)}. \quad (2)$$

Equation (2) corresponds to the physical picture of two condensers in parallel, whose capacities per unit area equal K_1 and K_2, and the areas they cover are proportional to the concentrations of anions and cations in Helmholtz's layer. Philpot in the paper mentioned above gave another method of uniting the positive and negative branches, which are expressed by Stern's equation with different values of K, into one whole, lacking a definite physical meaning, however. If we substitute the value of K from (2) in (1), it is not difficult to get the following relations from this equation:

$$\varphi = \psi_1 + \frac{2cdF}{K} \text{ sin hyp } \frac{\psi_1 F}{RT} + \frac{4c\lambda F}{K} \text{ sin hyp } \frac{\psi_1 F}{2RT} \quad (3)$$

$$\frac{\partial \varepsilon}{\partial \varphi} = KA : \left\{ A + K - \frac{1}{2}(K_1 - K_2) \frac{(\varphi - \psi_1)F}{RT} \cos \text{hyp}^{-2} \frac{\psi_1 F}{RT} \right\} \quad (4)$$

where

$$A = \frac{2cF^2}{RT}\left(d \cos \text{hyp } \frac{\psi_1 F}{RT} + \lambda \cos \text{hyp } \frac{\psi_1 F}{2RT}\right).$$

From equations (2), (3) and (4) a curve can easily be drawn which gives the capacity value $\frac{\partial \varepsilon}{\partial \varphi}$ as a function of φ. The curves in Fig. 2 were calculated in this manner, taking $K_1 = 38$ μF/cm² and $K_2 = 20$ μF/cm². The values on the abscissa axis in Fig. 2 are counted from the zero charge point. From comparing Figs. 1 and 2 it will be obvious that the general position and form of the curves calculated according to Stern's theory greatly resemble the experimental curves, but the calculated capacity values are situated considerably lower than the observed ones. Thus, for instance, the minimum of observed capacity for the 0.0001 n solution equals 3.9 μF, while calculation according to the equation (4) gives $\frac{\partial \varepsilon}{\partial \varphi} = 2.15$ and according

to Gouy's theory of the diffuse layer—2.36 μF. Thus, it may be concluded that the real double layer is less diffuse than should be expected according to theory.

This deviation shows that there are specific attractive forces, i. e. attractive forces which do not depend upon the charge, between the metallic surface and the ions. This adsorption effect, however, cannot be identical to that which is observed at higher concentrations. Indeed, high capacity values are observed to both sides of the zero charge point, i. e. the interaction mentioned should be ascribed to both cations and anions, while it is well known from electrocapillary data that at higher concentrations inorganic cations show negative and not positive adsorption. It must be assumed that we have to do here with attraction which turns into repulsion at short distances. It is possible that at large distances those image forces are manifested which were postulated by Gurney and which for reasons as yet unknown are not observed when the ions are in the immediate vicinity of the surface of the mercury electrode.

It is a pleasure to express our gratitude to M. A. Proskurnin for valuable suggestions and collaboration in doing this work.

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PHYSICAL CHEMISTRY

ON THE MECHANISM OF THE EXPLOSIVE DECOMPOSITION OF TETRYL

By A. J. APIN

(Communicated by N. N. Semenov, Member of the Academy, 23. VII. 1939)

The composition of the explosion products of explosive substances (e. s.) depends greatly upon the conditions of the explosion. In some cases for e. s. of varying density and for various initial impulses after cooling the explosion products under identical conditions («tempering»), attempts were made to explain the difference in composition from a purely thermodynamic point of view (1). These explanations are not altogether faultless in calculations and also as a result of the fact that a member of quite arbitrary assumptions were admitted.

When some explosive mixtures (ammonites, dynamite) were exploded in an evacuated steel bomb in a surrounding of sand, the composition of the gaseous explosion products differed pronouncedly from the composition of the gaseous products produced during the explosion of a freely hanging charge (not surrounded with sand). For instance, during the explosion of ammonite No. 2 (88% ammonium saltpetre and 12% trotyl) nitric oxide is produced in a quantity of about 50 l to 1 kg ammonite, while for the freely hanging charge nitric oxide is not produced at all (2).

If the equilibrium composition of the gaseous products at the moment of explosion is calculated for ammonite No. 2, then even under these conditions

Conditions of explosion	Density of explosive substances	Composition of gaseous		
		HCN and oth.	CO_2	NO
Powdered tetryl. Charge hanging freely .	~ 0.9	1.50	6.26	0.0
Powdered tetryl. Charge in a surrounding of white «soot»	~ 0.9	3.67	8.81	0.73
Large-grained tetryl. Charge hanging freely	~ 1.2	1.40	8.61	0.15
Large-grained tetryl. Charge in a surrounding of white «soot»	~ 1.2	5.42	14.55	0.51

maximum quantities of nitric oxide are almost ten times less than the quantities obtained by experiment. From the point of view of the «tempering» of the equilibrium explosion products this phenomenon is entirely inexplicable.

We performed several experiments with tetryl (tetranitromethylaniline), a well detonating explosive. For the experiments we took pulverized tetryl of approximately 0.9 density, large-grained, consisting 65% of crystals 2—3 mm in dimensions and 35% powder with an average density of app. 1. 2. The charge consisted of 9 g tetryl and a two-gram initiator (1 g tetryl pressed at 1 000 atm. and 1 g lead azide). The charge and initiator were 10 mm in diameter and were in a glass shell. The explosion was performed in an evacuated (app. 1 mm) steel bomb 4.8 l in capacity, with the charge hanging freely and with the charge placed in glass beaker filled with very fine pure silica powder (the white «soot» used in the rubber industry). About 140 g of silica powder was taken.

The gaseous products were analyzed by means of mercury Dreschmidt pipettes with a small quantity of absorbing liquid. Since HCN, C_2N_2 and NH_3 were present in the gaseous explosion products, the gas was treated with a 10% aqueous sulphuric acid solution, before CO_2 was absorbed.

The table gives the results of analysis for four tetryl explosions. It shows the pronounced influence of inert dust surroundings on the composition of the explosion products.

In view of such a composition and such large quantities of complex solid residue it is useless to try and explain the differences obtained only by the conditions available on «tempering» the equilibrium products of the explosion. Evidently, the inert dust mixes with the explosive substance during the very process of explosive decomposition, quickly enough to influence the mechanism of the decomposition.

We believe that the facts described above can be explained if we assume that the explosive decomposition of tetryl goes on not through the whole mass of the substance, but begins only at the surface of separate tetryl particles, and that the particles combust later on in the high temperature and pressure zone, whereby the function of ignition and crushing may be ascribed to the shock wave travelling through the explosive substance. Ignition is a result of contraction of the air inclusions and intervals between the particles, rather than of contraction of the substance itself ([3]). In this case even if the pressure drops are small, the temperature rises a lot.

explosion products in volume %				Residue in % to weight of tetryl			Specific volume of gases in l/kg
CO	CH_4	H_2	N_2	Moisture a. volatile products	Soluble in acetone	Insoluble in acetone	
56.60	0.82	12.38	22.44	0.5	—	2.5	834
54.86	1.28	6.61	24.04	2.0	1.5	3.2	743
52.90	1.10	12.36	23.48	0.6	0.5	3.8	798
46.36	1.18	6.26	25.72	2.6	4.0	9.2	658

Since the heterogeneity factor and the shock wave play such a part, two stages should be distinguished in the process of explosive decomposition: the stage of ignition of the shock wave and the stage of combustion proper of the separate particles in the zone of high temperature and pressure. From this point of view changes in composition are connected with the intervention of the inert dust in the process of combustion of scattering tetryl particles. Naturally, if there is intervention, the combustion of the particles will take place under different regimes, under regimes of incomplete decomposition. At a certain point, under energetic intervention, combustion may stop altogether. Change in the combustion regimes of the particles results in a change in the composition of the explosion products.

This mechanism may, possibly, underlie the decomposition of many other explosive substances and mixtures. If it is accepted for a wider variety of explosive substances, many of the phenomena, which were very difficult to explain up till now, become clearer; such are over-pressing, ageing of dynamites, low susceptibility to the initial impulse among fused explosive substances, the relation between the linear velocity of explosive decomposition and the charge density, the diameter and durability of the shell, etc.

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GEOCHEMISTRY

NEW DATA ON THE DISTRIBUTION OF INDIUM IN KAZAKHSTAN

By S. A. BOROVICK and N. M. PROKOPENKO

(Communicated by W. I. Vernadsky, Member of the Academy, 19. VII. 1939)

The Variscian cycle has played a most important part in the metallogeny of Kazakhstan. The first Variscian cycle which terminated during the Middle Carboniferous had been accompanied by intrusions, chiefly of granodiorite magma.

Kassin ([2]) refers to this cycle certain lead-zinc and copper deposits of East Kazakhstan. During the second Variscian cycle (Middle Carboniferous—Middle Permian) there have taken place intrusions of leucocratic well differentiated granites of the alaskaite type. With the second cycle is connected the formation of tungsten, tin and iron deposits, as well as that of the polymetallic and copper deposits of East and South Kazakhstan. There is a number of various deposits which are genetically connected in Kazakhstan: copper (Counrad, Bosche-kul, Dzhezkazgan), pyrite (Maikain, Berkara, Alexandrovskoye) and lead-zinc deposits (north-western near-Balkhash region, the Kara-tau range, the Djungar Alatau). Most of them belong to the mesothermal type. The zinc ores indium is chiefly associated with have been encountered in the following regions: 1) Dzhezkazgan-Kurgasyn, 2) Kara-tau, 3) Maikain Pribayanaul, 4) Berkara-Karkaralinsk, 5) north-western near-Balkhash area, 6) Djungar Alatau and 7) the Altai.

D z h e z k a z g a n-K u r g a s y n R e g i o n. Dzhezkazgan is one of the largest copper deposits of the meso-epithermal type. The principal ore-minerals are bornite and chalcopyrite; sphalerite is present only in small quantities.

A study of the distribution of rare elements and disseminated elements in Dzhezkazgan, formerly organized by the Institute of Geology and Mineralogy, has not given any positive results with regard to indium. Later in 1936 in the specimens collected by I. G. Chentzov, traces of indium have been found spectroscopically in the unfinished products and wastes of the Karsakpai copper-smelting works: in the slag and dust from the reverberating furnace flue, in the Dorr thickener tailings and in black copper. Besides, traces of indium have been established in the Naiza-tas deposit (in manganese ore, limestone, iron ore). The distribution of indium is very irregular and in a number of manganese ore specimens from this deposit indium is absent.

Traces of indium have been encountered in the specimens collected by Chukhrov, in cleiophane from Dzhezkazgan and in sphalerite from Kurgasyn.

K a r a-T a u R e g i o n. The majority of lead-zinc deposits are confined to the limestones of the Upper Devonian—Lower Carboniferous. The mesothermal Variscian lead-zinc deposits of the Kara-tau range (Achi-sai, Kantaghi, Kara-sai, Baidjan-sai, Suleiman-sai) are characterized by low indium concentrations. A higher indium content has been encountered in one of the specimens of brown sphalerites from Achi-sai (hole No. 91, depth 75.4 m). In three other sphalerite specimens from the same deposit indium has not been established, while germanium is present, usually in low concentrations.

In thousandths of fractions of a per cent indium has been established in sphalerites from Kantaghi and Kara-sai, in cleiophane from the Smena deposit as well as in the polymetallic ore from Baidjan-sai. The indium content is in general non-persistent and is far from being present in all specimens. Presence of germanium is more typical of the zinc blende from the Kara-tau range (Achi-sai, Kantaghi, Kara-sai) than that of indium.

In the oxidation zone of lead-zinc deposits the presence of indium has not been established in the material analyzed. In particular indium is absent in the minerals of Achi-sai (cerussite, galmei, smithsonite, calamine), Kara-sai (galmei) and Suleiman-sai (cerussite, calamine, vanadinite). Indium is absent in the lead concentrate and tailings of the Achi-sai concentrating mill, as well as in the lead concentrate from Kantaghi.

The zinc-sulphide ores of a number of deposits of the Kara-tau range (Kantaghi, Kara-sai, Baidjan-sai) may have practical importance for the recovery of indium and, possibly, germanium during the milling of these ores. Achi-sai, the largest deposit of the region, is represented by oxidized lead and zinc ores, in which the presence of indium has not yet been established. Sphalerite is encountered in this deposit as a mineralogical rarity.

M a i k a i n-P r i b a y a n a u l R e g i o n. Rather persistent is the presence of indium in the pyrite of the large gold-pyrite Maikain deposit (slight lines and traces). Low indium concentrations are rather frequently present in the jarosites of Maikain (F. V. Chukhrov). Indium seems to be more widely spread in the Maikain deposit than it is believed at present owing to desultory and incomplete data.

A further study of the Maikain for rare and disseminated elements is quite necessary.

B e r k a r a-K a r k a r a l i n s k R e g i o n. Traces of indium have been established (in connexion with the work of P. D. Fedorkov) both in the polymetallic ore from Berkara and in cerussite (low, occasionally somewhat higher concentrations).

N o r t h-W e s t e r n N e a r-B a l k h a s h R e g i o n. In this region both lead-zinc mesothermal deposits (Kyzyl-espe, Gulshad, Ak-chegyl, Aurora, Kara-tyube, etc.) and hypomesothermal deposits in skarns (Aksoran, Samenbet) are widely spread.

According to a spectroscopic analysis of the samples collected by P. D. Fedorkov, the presence of the following elements is typical of the polymetals of the north-western near-Balkhash region: molybdenum, bismuth, tellurium, cadmium, silver, tin, indium and gallium. Indium is a rather wide spread element in the polymetals of this region, it being encountered in higher concentrations in the sphalerites of certain deposits (Kyzyl-espe, Ak-chegyl). The north-western near-Balkhash region deserves as a whole attention with regard to indium, but of special interest is the deposit Kyzyl-espe which is of economic importance owing to its high indium content.

Indium has been established in 18 out of 77 specimens of different minerals from Kyzyl-espe.

Of great interest is the wide range of distribution of indium in Kyzyl-espe: indium has been encountered simultaneously in a number of different minerals of the sulphide complex, which in general is not frequently the case in nature.

Especially rich in indium are black sphalerites of the marmatite type. Indium is present also in thousandths of fractions of a per cent in chalcopyrite, pyrite, bornite, galenite and chalcozite (in bornite and galenite higher indium concentrations are sometimes encountered).

The second peculiarity of the Kyzyl-espe deposit is the dependence of higher indium concentrations in sulphide minerals (sphalerite, galenite, chalcopyrite, pyrite) on their tin content. Those minerals which contain more tin are, as a rule, characterized by a higher indium concentration, too. In ten galenite samples containing no tin, no indium has been found either. Attention is attracted by a considerable persistance of the presence of indium in a number of sulphide minerals from Kyzyl-espe. The development of indium in Kyzyl-espe is of practical importance and should be given proper attention.

In low concentrations indium is present in a number of other polymetallic deposits of the north-western near-Balkhash region: in Ak-chegyl, Aurora, Gulshad, Kuzy-adyr and Samenbet. High indium concentrations are encountered in zinc blende from Ak-chegyl, and those of gallium in sphalerite from the Aurora deposits. A number of polymetallic deposits of the north-western near-Balkhash region deserve practical attention on account of indium, since the latter may be recovered by means of a complex treatment of the ores from the deposits of this region. Especial attention should be given to the Kyzyl-espe deposit.

D j a n g a r-A l a t a u. The large mesothermal polymetallic Tekeli deposit is characterized by low indium concentrations. Indium in thousandths of fractions of a per cent is present sometimes in sphalerite, galenite and jarosite, but its presence is not persistent. Aside from indium, traces of thallium, germanium and gallium are also present in the polymetals of Tekeli (the presence of thallium has been ascertained in the Institute of Rare Metals).

A systematic study of rare and disseminated elements should be organized in the Tekeli deposit.

T h e A l t a i represents a geochemical province impoverished in indium. It cannot be said that indium is absolutely absent at the Altai. Its presence has been established in several deposits, but the concentration is very low and the distribution is non persistent. Pavlikov ([3]) has reported of traces of indium in the ores of the Ridder and Zyryanovsk; according to Pilipenko ([4]) indium has been encountered also in sphalerite from the Petrovsky deposit and in galenites from the Zyryanovsk and Berezovsk deposits.

Recently, Domarev ([1]) has shown the presence of indium in deposits of the Ridder type.

The study of the distribution of rare and disseminated elements in the polymetals of the Altai carried out by Shcherbina in 1936 involved a great number of spectroscopic analyses. There are only three specimens in which indium has been encountered in thousandths of fractions: in sphalerite and pyrite from the Zavodinsky deposit, in galenite from the same deposit and in tailings from the Ridder (after a preliminary chemical concentration of the latter). In the ores of the Belousovsky, Ridder, Zyryanovsk, Zmeinogorsk and Berezovsk deposits indium has not been detected.

The work carried out in 1938 at the Altai by the All-Union Geological Institute somewhat widened the area of distribution of indium in the lead-

zinc deposits of this region; yet it did not alter essentially the idea that had existed about the subject. In organizing further searches for indium in the region of Altai attention should be given to the deeper horizons of lead-zinc deposits, as well as to the high-temperature type of these deposits.

Summing up the data on the distribution of indium in Kazakhstan, three regions should be pointed out as already deserving practical attention; these are: the Djungar Alatau, the north-western near-Balkhash region and the Kara-tau range. Zinc ores in these regions may serve as raw material for the recovery of indium. In the course of further work other ores will surely be found, from which raw material will be supplied for the recovery of indium.

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MINERALOGIE

DIAMANTKRISTALLE VOM FLUSSE POLYDENKA AUS DEM BEZIRK TSCHUSOWSKOY

Von G. B. BOKY und G. G. LEMMLEIN

(Vorgelegt von A. E. Fersman, Mitglied der Academie, d. 4. VII. 1939)

Die in der Nähe der Bisert-Werke am Flusse Polydenka (mittlerer Ural) gefundenen Diamantkristalle wurden uns zur kristallographischen Untersuchung von G. V. Foss überlassen.

In diesem Bezirk wurden in 1829 Diamantkristalle gefunden und in den folgenden Jahren wurden über 250 Kristalle gesammelt (1). Sämtliche Kristalle besitzen rhombisch-dodekaedrischen Habitus mit gekrümmten Kanten, was für Diamanten typisch ist, insbesondere für brasilianische Diamanten. Die Abrundung der einzelnen Kristalle ist verschieden und nach diesem Merkmal können sie in Reihen geordnet werden. Für einzelne Kristalle ist eine tiefe Korrosion der Kanten charakteristisch. Wir beschreiben im Folgenden zwei besonders charakteristische Kristalle. Der eine bildet einen abgerundeten rhombischen Dodekaeder von isometrischem Habitus. Sämtliche Kanten dieses Kristalls sind stark korrodiert, weswegen einzelne Abschnitte der glatten sphärischen Oberflächen in Gestalt einzelner Inseln erscheinen (Abb. 1). Oft sind diese Inseln von abgerundeten Terrassen umgeben, während die Zwischenräume zwischen den einzelnen Inseln von Hügeln bedeckt sind, die sich längs der langen Diagonale des Rhombus erstrecken.

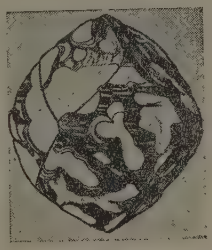

Abb. 1.

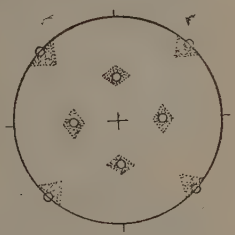

Abb. 2.

Abb. 3.

Abb. 4.

Im Goniometer erhält man deutliche Signale nur von den glatten Abschnitten der Kanten, d. h. von den Inseln. Die Zwischenräume geben in der Regel keine Signale. Die Spiegelung von diesen äussert sich nur in einer Aufhellung des Gesichtsfeldes.

Die Signale der sphärischen Kanten lagern sich in kontinuierlichen Feldern um Punkte, welche dem flachkantigen rhombischen Dodekaeder entsprechen. Der Umriss dieser Felder stellt in stereographischer Projektion einen sphärischen Rhombus dar, dessen Länge 20—40° und dessen Breite 20—30° beträgt (Abb. 2). Der Kristall besitzt drei Kanten, wobei eine jede durch zwei sphärische Flächen gebildet wird, die sich in Richtung der kurzen Diagonale schneiden. An dieser Stelle erscheint eine gekrümmte zusätzliche Kante.

Der zweite Kristall ist stärker abgerundet als der erste. Er besitzt ebenfalls rhombisch-dodekaedrischen Habitus, ist jedoch einwenig in Richtung der dreifachen Achse gestreckt (Abb. 3). Sämtliche Kanten sind nach der kleinen Diagonale des Rhombus durch zusätzliche Kanten unterteilt, weshalb man als einfache Form wohl den doppelt-pyramidalen Würfel annehmen muss, der allerdings dem rhombischen Dodekaeder sehr nahe ist.

Die Kristalloberfläche ist vollkommen glatt. Das eine Ende des gestreckten Kristalles zeigt Zwillingsstrichelung nach {111}. Man erhält deutliche Signale von den Kanten.

In der stereographischen Projektion fehlen Signale an denjenigen Stellen, die dem rhombischen Dodekaeder (flachkantigen) entsprechen (Kreise auf Abb. 4). In einem Abstand 2—4° von diesem Punkte nach beiden Seiten in Richtung der langen Diagonale beginnt ein kontinuierliches Feld von Signalen, welches sich auf 15—25° erstreckt. In senkrechter Richtung erstreckt sich dieses Feld auf 40—50°. Infolgedessen wird jede Kante des «rhombischen Dodekaeders» durch zwei dreieckige Felder von Signalen charakterisiert. In Abb. 4 sind sämtliche Felder gleich gross dargestellt (mittlere Grösse). In Wirklichkeit steht die Grösse des Feldes in direkter Abhängigkeit von der Grösse und der Krümmung der Kanten. Je kleiner die Kante, umso geringer ist das Signalfeld.

Beide Kristalle stellen anscheinend Auflösungskörper dar, wobei man jedoch zwei Phasen der Auflösung unterscheiden muss, eine ruhige, welche glatte Flächen und gekrümmte Kanten liefert, und eine stürmische, welche die Kristalloberfläche stark korrodiert.

Man kann annehmen, dass die Wachstumsform des Diamanten, der Oktaeder, während der ruhigen Auflösungsphase, indem er sich von den Kanten auflöst [(²), Abb. 101, 102, 103 u. 105], einen schiefkantigen rhombischen Dodekaeder bildet, wobei die Krümmung der Kanten mit der weiteren Auflösung zunimmt. Zu einem bestimmten Zeitpunkt tritt ein Übergang der Kanten des rhombischen Dodekaeders und Umwandlung desselben in einen pyramidalen Würfel ein.

Wenn eine derartige Auflösung auch weiterhin stattfindet, so müssen die Kristalle endlich kubischen Habitus annehmen. Kristalle, welche eine Reihe derartiger Übergänge zu der definitiven Auflösungsform des Diamanten, dem Würfel, zeigen, sind in der Monographie von A. E. Fersman u. W. Goldschmidt dargestellt [(²), Abb. 39, 64 u. 65].

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MINERALOGY

CHEMICAL-PHYSICAL INVESTIGATION OF ALUNITE FROM THE ZAGLIK DEPOSIT (TRANSCAUCASIA)*

By MIR-ALI KASHKAI

(Communicated by F. J. Loewinson-Lessing, Member of the Academy, 21. VII. 1939)

From its ore-reserves the Zaglik alunite deposit occupies the second place in the world, the first being given to the well-known maritime Fanshan deposit in south-west China. It is located 35 km south-westward of the town of Kirovabad (Azerbaidjan) and occupies the high mountain Sharu-kar (2098 m) between the villages of Verkhny Dashkesan and Zaglik. The deposit is located at the northern limb of the large flat-dipping synclinal fold with a latitudinal strike. In the southern part of the alunite beds porphyrites and their tuffs of the Upper Jurassic age may be distinguished, farther south-west in the area of the Dashkesan deposit they are replaced by granodiorites which caused the formation of a number of ores (magnetic iron ore, cobaltite, polymetals, etc.). From the north-east to the north-west along the alunite deposit, to the village of Zaglik, porphyrites stretch with their tuffs of the Middle Jurassic age.

Within the area of the deposit rocks of the Upper Jurassic age are widely developed. Coral limestones overlain by alunitized rocks are referred from the rich fauna found in them by Paffenholz (1) and Bushuev (2) to the Lusitanian substage. The tuffs, tuffobreccias and tuffites have been subjected to alunitization. The tuffs are a typical rock with a clastic structure approaching that of pseudoporphyres (chemical analysis No. 1). The chief components of the rocks are altered plagioclase, quartz, kaolin, haematite and porphyrite grit. In consequence of metamorphism the alunitized rocks, bearing the character of individual layers up to twenty in number, differ from each other in structure, percentage of mineral components and colouring, according to the grade of metamorphism.

Among these rocks, especially in the western part of the deposit, there are encountered veins of compact kaolin about 2—2.5 m thick. Kaolin presents a compact grey mass of green and violet tint (anal. No. 2). It also plays a great rôle in the mineralogical composition of the alunitized rocks. Refraction indices of kaolin: $Ng=1.567$; $Np=1.561$; $Ng-Np=0.006$. An interesting variety of a friable, asbestos-like, fibrous snow-white halloysite (anal. No. 3) has been found in the thin fissures (2—5 mm) of alunitized rocks. Its crystals are characterized by a direct extinction and positive elon-

* This deposit has been described in detail by the same author in his article entitled «Alunitization and kaolinization at the Zaglik deposit» (Transactions of the Azerbaidjan Branch of the Academy of Sciences of the USSR).

gation. Refraction indices of this mineral: $Ng=1.544$; $Np=1.536$; $Ng-Np=0.008$.

The results of a physical-chemical study of these two kaolin minerals carried out by Beliankin and Ivanova (who kindly undertook the thermal investigation of our material) are published elsewhere ([4]).

From the heating and dehydration curves it may be seen [for more details see ([3]) and ([4])] that the thermal curve of halloysite is distinguished from that of kaolinite only by an endothermal stop within the 50—110° temperature interval. This stop usually fails to be observed on the heating curve of kaolin owing to the insignificant amount of water isolated at 100° C. A thermal analysis showed that the crystalline halloysite from the Zaglik deposit is a typical kaolin somewhat hydratized (table).

Chemical Analysis of Alunites, Kaolin Minerals and Tuffaceous Rocks

Components in weight %	Tuffaceous rock of Zaglik	Kaolin of Zaglik	Halloysite of Zaglik	Alumi-nite near Gaal (Saxon province)	Alunite (powder) Zhuravlinsk	Alunite of Zaglik	Spectroscopical analysis of Zaglik alunite*
1	2	3	4	5	6	7	8
SiO_2 . . .	62.90	45.54	43.20	0.98	0.02	1.81	Ga—0.005
TiO_2 . . .	traces	none	none	—	—	traces	Sn—not detect.
Al_2O_3 . . .	22.20	39.50	38.26	30.54	37.33	36.41	Pb—do
Fe_2O_3 . . .	4.80	0.06	none	none	none	1.06	Cu—weak lines
Feo	0.75	none	none	none	—	0.23	Mg—mean lines
MnO . . .	0.03	—	—	—	—	0.02	Ca—do
CaO	1.30	none	0.22	0.86	0.34	0.13	—
BaO . . .	—	—	—	—	—	0.04	Cr—weak lines
MgO . . .	0.90	0.06	traces	0.05	0.24	0.08	Zn—not detected
K_2O	4.10	traces	—	—	9.76	7.51	Cd—do
Na_2O . . .	2.35	—	—	—	0.98	3.89	Ag—do
$H_2O_{-100^\circ}$ . .	2.30	0.22	4.48	22.53	0.05	0.41	—
$H_2O_{+100^\circ}$ . .	1.15	14.44	14.28	24.00	13.13	9.90	Ni—weak lines
SO_3	0.70	—	—	21.20	37.93	38.79	—
CO_2	—	0.07	0.17	—	—	traces	Co—not detected
	100.58	99.89	100.61	100.16	99.78	100.28	
Analyzer	M. A. Kashkai	V. A. Moleva	M. A. Kashkai	Geol. Inst. Leningr.	N. A. Smolyaninov	M. A. Kashkai	

The richest area of the alunite deposit is the south-eastern part where the thickness of the alunitized rocks attains 45 m; westward the beds are gradually thinning out (up to 1—1.5 m); in the central and northern part the thickness averages about 25 m. It is of interest to note among certain types of alunitized rocks the presence of the isotropic mineral zunyite with a refraction index $Nm=1.590—0.001$.

The alunites found in the rock show sizes from microscopic scales up to large inclusions 6 cm in diameter (amygdales). Owing to their shape and

* Spectroscopical analysis made in the Spectroscopical Laboratory of the Geological Institute of the Academy of Sciences by S. A. Borovick.

arrangement the rock assumes a breccia-like character. Alunite is a pseudomorph feldspar or else a product of hydrothermal formation (large packets and bands of pure alunite). Alunite from the Zaglik deposit is characterized by the following physical properties: refraction indices: $Ng=1.5953$; $Np=1.5831$; $Ng-Np=0.12$; specific gravity of alunite—2.7; specific gravity of alunitized rocks—2.81.

In order to ascertain the chemical composition of alunite of the Zaglik deposit the author has made a chemical analysis of the pure mineral carefully isolated from a packet (anal. No. 6). The data of chemical analysis in terms of mineralogical composition are as follows: $K_2O \cdot 2.5\,Al_2O_3 \cdot 3.5\,SO_3 \cdot 4H_2O$—potassium alunite—56%; $Na_2O \cdot 2.5Al_2O_3 \cdot 3.5SO_3 \cdot 4H_2O$—sodium alunite—44%. A certain amount of SiO_2 not characteristic for alunite is accounted for by a fine dissemination of this component as quartz in the body of the mineral under investigation. A spectroscopic analysis shows the absence in it of a number of elements, except the isomorph of Al, weak Cr lines and the geochemically combined with Al element Ga (0.005).

The character of decomposition of the Zaglik alunite has been studied by Effendi and Negreev (5), Dementyev and Lutzenko.

At the author's request the alunites from the Zaglik (Fig. 1, anal. No. 6) and the Zhuravlinsk (Fig. 2, anal. No. 5) deposits, as well as the aluminite (Fig. 3, anal. No. 4) from the deposit near Gaal (Saxon province) have been subjected to a thermal analysis by Ivanova at the Laboratory of High Temperatures of the All-Union Geological Institute (Leningrad); the author avails himself of this opportunity to express her his gratitude*.

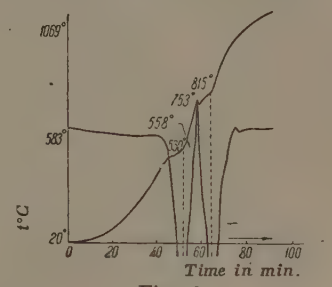

Fig. 1.

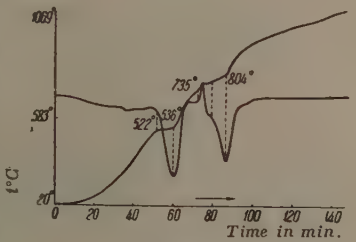

Fig. 2.

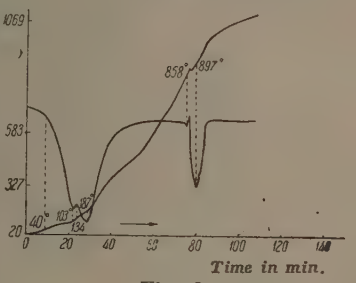

Fig. 3.

An interpretation of these curves shows that the endo- and exothermal reactions which take place during heating are intense and typical to such an extent that they may be recorded definitely and clearly on simple heating curves. On the differentiation curve the temperatures at which the reaction begins and comes to its end stand out more conspicuously. The heating curves of the first two samples show a complete similarity. When heated from 20 to 530° C alunite does not suffer any changes and the differential curve shows no deviations from its initial position. At 520° (525°) a sharp drop is observed corresponding to the endothermal reaction. This reaction is very intense and most sharply pronounced in the specimen from the Zaglik deposits. After the endothermal reaction has come to an end, at 735° (753°) a sharp jump of the differential curve is observed, corresponding to the exothermal effect, taking place within a

* The record of the temperature curve of the substance according to time has been made by means of a Kurnakov pyrometer.

narrow temperature range. Immediately after the exothermal reaction, an inflexion is recorded on the heating curve corresponding to the endothermal reaction which ends at 804—815°C. After this reaction the heating curve of the specimen heated to 1100° C shows no other thermal effects. Contrary to the heating curves of alunites, two low endothermal effect temperatures are recorded for aluminite (anal. No. 4), while at 853° a high temperature exothermal effect takes place passing to a very intensive endothermal reaction.

From the above thermal investigations the conclusion may be made that during the first endothermal reaction separation of water takes place, whereas during the second endothermal reaction separation of SO_3 and decomposition of the substance is observed.

According to Fink, Van Horn and Pahour (5.1248) and Alimarin and Podvalnaya (7.129), a synthesis of a portion of the sulphate of alumina and alkali to alkaline aluminite takes place during the final decomposition of alunite.

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PETROGRAPHY

ON THE GIGANTIC AEGIRITE-AUGITE CRYSTALS FROM THE PLUTONIC ROCKS OF GREMYAKHA-VYRMES (KOLA PENINSULA)

By A. A. POLKANOV

(Communicated by F. J. Loewinson-Lessing, Member of the Academy, 15. VII. 1939)

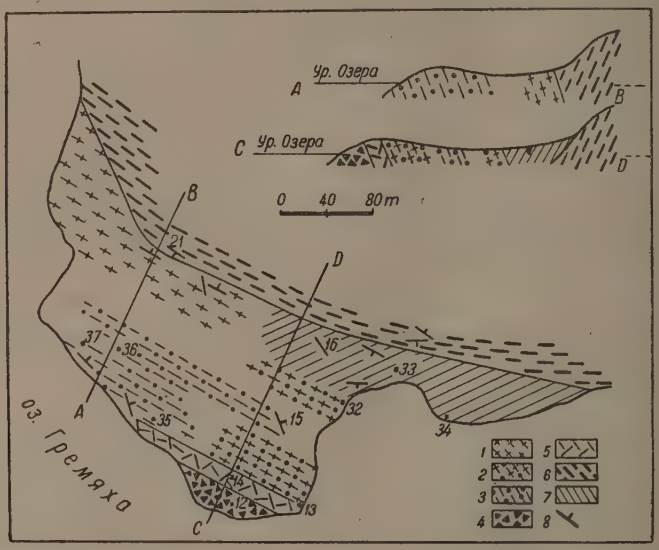
1. The plutonic rocks of Gremyakha-Vyrmes located in the north-western part of the Kola peninsula are a complex intrusive body formed during three intrusive phases: a) the phase of gabbro-syenite intrusion, b) the phase of nephelite-syenite intrusion and c) the phase of alkaline granite intrusion. The nephelite-syenites penetrate the middle portion of the plutonic rocks, forming two principal (and a number of smaller) bodies which constitute the Vyrmes «Varaka» (hill) and the Aegirite «navolok» or promontory on the lake Gremyakha. Gigantic aegirite-augite crystals have been found by the author at the Aegirite navolok ([1],[2],[3]).

2. The pluton of the nephelite rocks of the Aegirite navolok is a very complicated structure, as it may be seen from the figure. The remains of a block of ancient gneiss-granites and gabbro of the first phase of intrusion, as well as younger alkaline granites and syenites of the third phase of intrusion are adjoining it in the north. A small part of the pluton of nephelite rocks which remained intact is composed of foyaites, alkaline syenites, aegirinites and gigantic-grained ijolite-urtite-pegmatites.

3. Rather large aegirite-augite crystals have already been found in alkaline syenites adjoining the aegirinites (the south-eastern part). But they are especially large-sized in the south-eastern part of the aegirinite band forming these subparallel attachments along the *C*-axis, which show a similar orientation over considerable areas. Thus, within an area of 4 m² (according to additional observations made by N. A. Elisseev in an exposure) subparallel aegirite-augite attachments show an orientation of the vertical axis at 65° and an angle of incidence at 22—23°. Other areas of subparallel aegirite-augite attachments display a different orientation, persisting over smaller exposed areas.

4. In the gigantic-grained ijolite-urtite-pegmatites the gigantic subparallel aegirite-augite attachments are frequently up to 30—50 cm long. The nephelite crystals in the ijolite-urtite-pegmatite might probably have attained gigantic dimensions, too. However, we failed to observe this owing to a complete decay of this mineral transformed to an aggregate of secondary products. However, the grain size of the ijolite-pegmatite is as a rule highly variable; for aegirite-augite it does rarely exceed 1—2 cm in length.

Aside from this, loose huge blocks of subparallel aegirite-augite attachments have been observed at the shore of the lake Gremyakha, i. e. not in country-rock exposures. Since the nephelite-ijolite-urtite of the pegmatites is completely broken up (partly spreusteinized), it may be supposed that these huge attachments of aegirite-augite crystals might have been freed



Lake Gremyakha. Aegirite navolok (cape): 1—Alkaline granite. 2—Alkaline syenite. 3—Foyaite. 4—Ijolite-urtite-pegmatite. 5—Aegirinite. 6—Gabbro. 7—Gneisso-granite. 8—Strike and dip of directive and banded structures.

after the decomposition of the leucocratic portion of the gigantic-grained pegmatite. On the other hand, since the aegirinite body is dipping to the north-east, the aegirite-augite crystals might have been fallen out of the decayed aegirinite which was previously covering the ijolite-urtite-pegmatite body.

Table 1

	%	Mol. equiv.
SiO_2	50.03	833
TiO_2	0.72	9
Al_2O_3	3.27	32
Fe_2O_3	18.47	232
FeO	9.07	126
MnO	0.84	11
MgO	0.80	20
CaO	8.40**	150
Na_2O	7.62	123
K_2O	0.10	1
Losses on ignition	0.85	
H_2O hygrosc.	0.16	
	0.00	
V_2O_5	100.33%	

* Direct determination.
** Second determination CaO=8.35%.

5. One of such crystals or subparallel attachments of aegirite-augite, 110×35×20cm in size, has been found by the author and is kept now at the Chernyshev Geological Museum (in the Geological Institute) (in transit one end has been broken off, so that at present the length of the crystal is about 100 cm) The outer surface of the specimen has no natural crystal growth faces and is formed by cracks along the prismatic cleavage planes of aegirite-augite or occasional splittings due to frost weathering. Therefore,

the shape of the specimen is connected only with an elongation along the vertical axis of aegirite-augite.

The results of a chemical analysis of the specimen made by V. M. Frenkel (analyst to the Central Scientific Research Geological Prospecting Institute) are shown in Table 1.

Under the microscope it is seen that $NpC = 9°$; polychroism along Np and Nm—dark-green, along Ng—greenish-yellow. The thin-section shows that the aegirite-augite encloses minute albite grains, less frequently nephelite, carbonate, biotite and microcline. A calculation of the analysis for mineralogical composition gave the results shown in Table 2.

Table 2

	Fe_2O_3	NaO	SiO_2	Al_2O_3	K_2O	MgO	FeO	CaO	Mno	Σ,%
Acmite	18.47	7.06	27.90	—	—	—	—	—	—	53.54
Albite	—	0.56	3.26	0.92	—	—	—	—	—	4.75
Orthoclase	—	—	0.38	0.11	0.10	—	—	—	—	0.59
Chermak's silicate	—	—	1.19	2.02	—	0.80	—	—	—	4.02
$FeSiO_3$	—	—	7.61	—	—	—	9.07	—	—	16.67
$CaSiO_3$	—	—	9.03	—	—	—	—	8.40	—	17.43
$MnSiO_3$	—	—	0.71	—	—	—	—	—	0.84	1.55
	18.47	7.62	50.08	3.05	0.10	0.80	9.07	8.40	0.84	98.55

In calculating there was a lack of 0.05% SiO_2; 0.22% Al_2O_3 and 0.72% TiO_2 remained and the losses on ignition were 0.85%. Thus, it may be taken to mean that the sample analyzed contained 93.21% aegirite-augite, and 4.75% albite and 0.59% orthoclase as admixtures. The recalculated composition of aegirite-augite is given in Table 3.

Table 3

a		b
56.77% acmite		SiO_2—49.50%
17.67% $FeSiO_3$	hedenbergite	TiO_2— 0.76%
18.48% $CaSiO_3$		Al_2O_3— 2.15%
4.69% Chermak's silicate		Fe_2O_3—19.67%
		FeO— 9.66%
1.63% $MnSiO_3$		MnO— 0.89%
0.75% TiO_2		MgO— 0.84%
		CaO— 8.95%
99.99%		Na_2O— 7.54%
		99.96%

According to the optical constants, the aegirite-augite contains 58% acmite which fully agrees with the results of calculation of the chemical analysis (6). A petrological study of the nephelite rock complex of the Gremyakha-Vyrmes pluton shows that a 58% content of the acmite molecule is distinctive of the aegirite-augite of the yuvite and foyaite rock types (and the magma) of this pluton (3).

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CALCULATION OF THE ACTIVATION ENERGY AND HEAT OF FUSION OF FELDSPARS AND PYROXENES FROM VISCOSITY MEASUREMENTS

By M. P. VOLAROVICH

(Communicated by F. J. Loewinson-Lessing, Member of the Academy, 15. VII. 1939)

One of the characteristic physical properties of silicate melts is their high viscosity which is the cause of their crystalling poorly. It seemed interesting to apply the modern theory of viscosity of liquids to express the relation between the temperature and the viscosity of fused silicates, particularly of the main rock-forming minerals—feldspars and pyroxenes. The theory of viscosity of liquids is still at a comparatively low stage of development and not until recent years was the following equation obtained by various authors using various methods ([1–5]):

$$\eta = Ae^{\frac{B}{RT}} \qquad (1)$$

where η is the viscosity; T, the absolute temperature; R, the gas content; A and B, constants. This equation has then been used more than once as an empiric formula for expressing the relation between the temperature and

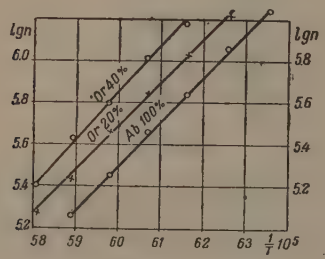

Fig. 1.

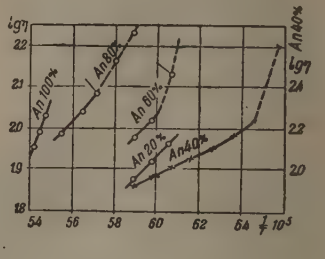

Fig. 2.

the viscosity of liquids. Its deduction is referred to in more detail in ([6]), where it is shown that formula (1) can be applied to fatty acids and triglycerides. It should be noted that A. A. Leontieva ([7]) applied equation (1) to a number of glassy borates, phosphates and silicates. Preston and Seddon ([8]), Taylor ([9]) and Stanworth ([10]) with a similar formula at hand arrived at a series of conclusions on the structure of glass.

Equation (1) is interesting because it makes it possible to imagine the nature of the intermolecular forces acting in the liquid, and also because,

according to the opinion of many authors, confirmed by experimental data, B is close to the heat of fusion L for a number of liquids of a definite type and proportional to L for substances of other types. Formula (1) can be checked for melts of feldspars and pyroxenes on the basis of the data on the viscosity of these minerals obtained by Kani and Hosokawa ([11]). Fig. 1 gives the results for albite and mixtures of albite and 20 and 40% orthoclase; $\frac{1}{T} \cdot 10^{-5}$ is plotted against the decimal logarithm of the viscosity; at the right there is a scale for 100% Ab, and at the left, for mixtures Ab—Or. As may be seen, in accordance with equation (1) straight lines are obtained in this co-ordinate system. The same kind of rectilinear graphs are obtained for other mixtures of the system Ab—Or and also for anortite and diopside and mixtures of the system Ab—An. Systems Di—An, however, give two intersecting straight lines, as may be seen from Fig. 2, where a scale for a mixture of Di with 40% Ab is plotted along the ordinate axis on the right, and for mixtures with other percentage correlations and for 100% An, on the left. The same kind of pairs of intersecting straight lines were obtained for mixtures of the binary system Di—Ab and the ternary system Di—Ab—An. No inverse angles of inclination of the straight lines was ever observed for feldspars and pyroxenes, though it is sometimes the case with the ordinary liquids.

On the basis of Bernal-Ward's theory it should be considered that the co-ordination number of melts which are characterized by one straight line remains constant, and the nature of the interaction between the molecules does not vary with the temperature. According to Bernal, the co-ordination number determines the average number of molecules neighbouring any given molecule. For liquids at room temperatures the co-ordination number is usually determined by X-ray analysis.

In the case of melts with two intersecting straight lines the co-ordination number, according to Bernal-Ward, changes at the point of intersection.

Table 1

% Ab	B, $\frac{\text{kg cal.}}{\text{mole}}$	Temperature interval, °C	% Ab	B, $\frac{\text{kg cal.}}{\text{mole}}$	Temperature interval, °C
System Ab—Or			System Ab—Di		
100	96,3	1425—1300	100	96.3	1425—1300
80	98.5	1450—1325	80	36.5	1425—1300
60	101	1450—1350	60	34.5	1425—1325
40	105.5	1450—1350	40	41	1425—1320
20	110	1450—1375	20	20	1425—1375
0	112	1450—1400	0	36.7	1425—1400
System Di—An			System An—Ab		
% Di			% An		
100	36.7	1425—1400	100	64.0	1575—1555
80	22.9	1425—1375	80	48.0	1550—1475
60	21.7	1425—1325	60	91.5	1500—1425
40	18.3	1425—1400	40	96	1425—1325
20	27.3	1525—1475	20	105	1425—1275
0	64.0	1575—1555	0	96.3	1425—1300

Table 2

Ternary System Di—Ab—An

Composition of mixtures in weight %			B, $\frac{\text{kg cal.}}{\text{mole}}$	Temperature interval, °C
Di	Ab	An		
60	20	20	25.2	1425—1325
20	20	60	71	1425—1375
40	40	20	64	1425—1250
40	20	40	50.5	1425—1350
20	40	40	75.5	1425—1325
20	60	20	82.5	1425—1250

In this connexion the activation energy B, determined by the incline of the line, is constant throughout the whole temperature interval for melts which show only one straight line. If there are two straight lines, however, the activation B is different for higher and lower temperatures. Usually, B is greater at low temperatures than at high ones. It should be noted that the intersection points of the straight lines sometimes do, but mostly do not coincide with the initial temperature of crystallization of the melt; the latter is shown in Fig. 2 by means of arrows.

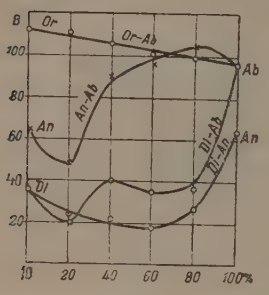

Fig. 3.

The values of B calculated from graphs for binary systems of feldspars and pyroxenes are given in Table 1, and for a ternary system in Table 2. It must be noted that for mixtures «mole» should be understood conventionally.

As has been mentioned above, the value B is of interest because, according to Bernal-Ward, it is simply related to the heat of fusion of the substance. Until recently the heat of fusion of silicates was determined by indirect methods on the basis of their heats of solution. Only of late was Roberts ([12]) successful in determining the heat of fusion of one silicate—Na_2SiO_3—by a direct method. V. Eitel ([13]) gives the following values of crystallization heat for feldspars and pyroxenes from Müller's data in kg cal./mole: Or—61.1; Ab—25.4; An—29.0 and Di—22.0. These are rather the heats of solution of the minerals in hydrofluoric acid; the respective correction has been made for them for the transition from 18° to the melting temperature.

Comparing the above values of L with the corresponding value of activation energy B given in Table 1, the ratio B/L can be found: for orthoclase it is 1.8; for albite, 3.8; for anortite, 2.2; and for diopside, 1.7. Taking into account the approximate nature of these calculations, it may be concluded that the heats of fusion of feldspars and pyroxenes are about twice as small* as their activation energies given in Table 1.

Thus, it should be considered that only half of the activation energy of these minerals is spent during a viscous shift on breaking the intermolecular bonds in the same way as during fusion. What accounts for the rest of the value B is possibly the energy of Van-der-Waals' intermolecular reaction of another kind of bond destruction. In this connexion it is inte-

* It may be considered that for albite the experimental figure of the heat of fusion is smaller than it should be.

resting to note that the activation energy of the very viscous glass-like oxides SiO_2 and B_2O_3, whose melts evidently have a special structure, is tens of times greater than the heat of fusion. Thus, for SiO_2 the heat of fusion ([13]) equals only 2.21 kg cal./mole, and the activation energy B=153 kg cal./mole; for B_2O_3 the heat of fusion L, according to the data of Kracek, Morey and Mervin ([14]), equals 97 cal./mole or 6.75 kg cal./mole, while the activation energy is close to 70 kg cal./mole. Evidently, in the melts of these oxides during viscous flowing a special kind of bonds are ruptured. These are possibly chemical, valency bonds, whose rupture requires a large amount of energy.

Furthermore, it seems interesting to examine the variations of the value B for binary systems given in Table 1. Fig. 3 represents a diagram of the activation energy of these double systems; the percentage concentrations by weight of the respective components are plotted along the abscissa axis. Curiously enough, a straight line is obtained for the system Ab—Or in Fig. 3. For other systems the relation is considerably more complex.

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HISTOLOGY

EXPERIMENTAL STUDY ON THE DEVELOPMENT OF MOLLUSCS IN CONNEXION WITH THE PROBLEM OF PHYSIOLOGICAL GRADIENTS

By G. STRELIN

(Communicated by I. I. Schmalhausen, Member of the Academy, 9. VII. 1939)

C. M. Child (4) has devoted a number of studies to the problem of domination and subordination in the correlation between different parts of organisms. These studies speak in favour of the notion that physiological gradients play the rôle of the organism's «prenervous connexions». The localization of the nervous system in the organism both in vertebrates and invertebrates, and the prevalence of the phenomenon of physiological gradients in the animal realm also corroborate indirectly the idea of the gradients as of elementary systems which integrate the organism.

Proceeding from this conception of gradients it could be expected that, contrariwise to the animals with a regulatory type of development, in which the presence of axial gradients at the early stages of embryonic development has been observed by numerous authors, it would be possible to establish the presence of a physiological mosaicity in the animals with a mosaic type of development, which have been but little studied in respect of gradients (3). This might be bound, on the one hand, with the acquisition of a definite specificity by different rudiments determined already in the early stages of development, on the other, with the correlative autonomy of the development of these rudiments. One could suppose consequently that in the case of mosaic development no axial gradients would be detected.

I conducted a study in the line on the development of molluscs belonging to the classes of *Amphineura* (*Chiton marginatus* Pennat), *Lamellibranchia* (*Loripes lacteus* L., *Syndesmia ovata* Phil., *Teredo navalis* L., *Ostrea taurica* Kryn., *Anodonta anatina* L.) and *Gastropoda* (*Cerithium ponticum* Mil., *Nassa reticulata* L., *Limnaea stagnalis* L., *Physa fontinalis* L., *Planorbis corneus* L.) using for this study three methods previously applied by Child in his researches.

The physiological unhomogeneity of the embryos was observed in experiments with: 1) the differential destruction of various sections of the embryo under the influence of injury-producing factors (brilliant-cresol-blue, ethyl alcohol, KCN and some others); 2) the differential suppression of the development of the different sections of the embryos in experiments with their exposure to a relatively weak or short-lived action of injury-producing factors; 3) the differential capacity of the different parts of the embryos to reduce the oxidation-reduction indicators in the course of intravital staining under conditions of asphyxiation. Experiments were made on embryos taken at various stages of their development, beginning with the stage of the fertilized egg-cell.

The results of the experiments with agents which led rather soon to a destruction of the cells and tissues of the embryo showed that some sections of the embryo are destroyed sooner than the others. The difference in the sensitivity of the different sections is in some cases (*Anodonta*) so great that after the elimination of the injurious agent only a definite section of the embryo is found to be destroyed, while all the rest remains alife and continues developing.

It proved possible to find by means of this method that in all molluscs, the embryonic development of which leads to the formation of a trochophore larva (*Chiton*, *Loripes*, *Syndesmia*, *Teredo*, *Ostrea*, *Cerithium*), a rather high sensitivity is shown at this stage of development by the pretrochal zone of the larva. This zone is destroyed first, while the posttrochal section disintegrates but later. A similar distribution into more and less sensitive sections is manifest already in the egg-cells of these forms. Within the limits of each zone, both of the more sensitive and of the less sensitive one, we failed to detect a sequence in the destruction of their parts which would be connected with the main axis of the embryo. The animal part of the embryo appears as an individual rudiment distinguished by a relatively high sensitivity level. The posttrochal zone also seems uniform in respect of sensitivity.

In the forms with a reduced trochophore (*Anodonta*, *Limnaea*, *Physa*, *Planorbis*, *Nassa*) the animal part of the egg as well as that of the embryos at later stages of development shows no heightened sensitivity. Thus, in none of the forms studied the animal-vegetative axial gradients of sensitivity could be detected in the course of their development.

The particularly high resistance of the prototrochon's cells bearing the ciliae to the action of injury-producing factors may be also connected with the specific differentiation of the individual rudiments. In *Limnaea* it is possible to demonstrate a relatively greater resistance of the trochoblasts beginning with the moment of their segregation, i. e. at the stage of 16 blastomeres.

The vegetative zone of the egg-cell and the macromeres at the beginning of segmentation show a relatively high sensitivity in all the *Gastropoda* studied (*Nassa*, *Cerithium*, *Limnaea*, *Physa*, *Planorbis*), and in them only. In *Nassa* this sensitivity of the vegetative pole is expressed in that the polar lobe is destroyed earlier that the rest of the embryo; at later stages of development the macromeres of the quadrant *D* prove more sensitive than the macromeres of other quadrants. The high sensitivity found in the *Gastropoda* seems to be connected with a special differentation of the entodermal rudiment. In *Anodonta*, in which we investigated the differential sensitivity of the oocytes also, at this stage of development of the sexual cell the vegetative pole appears to possess a prevalence in sensitivity. Later on with the beginning of segmentation a particularly elective and high sensitivity is shown by the blastomere *D* and still later by 2 *d*, which is the rudiment of the conch gland and the flittering field.

Under certain conditions differentially injured larvae continue, as it has been mentioned above, their development, defectuous glochidiae being found at the later stages of development, which lack the conch and the flittering field. At the same time a half-destroyed dead cell is found within the capsule—the blastomere 2 *d*, isolated after it had been injured at the beginning of segmentation.

By the method of differential suppression of development by means of exposition to a weak or short-lived action of the injury-producing agents it is also possible to demonstrate this physiological mosaicity of the embryos in some cases. The embryos of *Chiton*, being subjected to conditions which are not optimal for them (Caspian Sea water), are transformed into malformed trochophore larvae, in which the pretrochal zone lags greatly

behind in its development and the eyes as a result are relatively closely set. In *Nassa* after a short-lived exposure to the action of 2.5—5% alcohol on its egg-cell, the formation of the polar lobe is suppressed; in connexion herewith the macromeres *D* formed after the segmentation of such egg-cells are not distinguished by a greater size from the normal ones. At the early stages of segmentation in *Nassa* the segmentation of the more sensitive vegetative zone is suppressed; in connexion with this the segmentation proceeds atypically and reminds one of discoidal segmentation. Exposure to weak injury-producing factors suppresses differentially the segmentation of the more sensitive blastomeres 2 *d* in *Anodonta*. The results of these experiments perfectly agree with those obtained in experiments with poison concentrations which rapidly destroy cells and tissues.

The experiments with the reduction of the oxidation-reduction indicators showed, like those in which the differential sensitivity of the embryos was studied, that no physiological gradients can be found in the course of the development of molluscs. In the different sections of the intravitally stained embryos the stain is reduced at different rates; the ability to rapidly reduce the stain is far from frequently coincide with the high sensitivity of the respective section. Consequently, there is no parallel dependence between the level of sensitivity to poisons and the rate of reduction. This circumstance, at variance with Child's general conception and its explanation, seems to lie in the specific differentiation of the individual rudiments of mosaic eggs; however, these facts can be also accounted for in another way (2).

In general the distribution of the zones, reducing the stains rapidly or at a relatively low rate, presents a motley picture, and the positive moment of the results obtained by researches on the reduction of indicators is the mosaic character of the rate of this reduction in almost every of the forms studied, which is observed already at the early stages of their development.

The animal zone of the egg and trochophore shows the ability to reduce stains at a relatively high rate in *Chiton* only. However, in this case likewise the gradient of reduction, in the shape of a gradual decrease of the ability to reduce stains along the axis of the embryo, is absent. In *Loripes*, *Ostrea* and *Cerithium* the vegetative zone possesses the ability to reduce stains more rapidly than the animal one at the beginning of development, similarly to what has been described for *Aplysia* by Ries and Gersh (1). The macromeres of the quadrant *D* in *Nassa*, as well as the blastomeres *D* and 2*d* in *Anodonta* which exhibit a high elective sensitivity to poisons, reduce the indicators at a slower rate than the other sections of their embryos. In *Limnaea* and *Planorbis* at the stages of segmentation the reduction of stains lacks completely its differential character.

The totality of these data obtained by three different methods of research, permits to establish a clear-cut distinction between the animals with a regulatory and those with a mosaic type of development. No axial gradients are detected at the various stages of embryogenesis in the case of mosaic development. Quite opposite is the case in the physiological respect: the embryo presents a kind of a mosaic which should be referred to the early determination and specific differentiation of the various embryonic rudiments. The absence of axial gradients in the development of mosaic eggs corroborates indirectly the rôle of gradients as of systems which integrate the organism.

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HISTOLOGY

DETERMINATION AND PHYSIOLOGICAL CHARACTERISTICS OF THE RUDIMENT OF THE CONCH-GLAND AND THE FLITTERING FIELD OF *ANODONTA ANATINA* L.

By G. STRELIN

(Communicated by I. I. Schmalhausen, Member of the Academy, 9. VII. 1939)

An early determination of rudiments in the case of the so-called mosaic development testifies, on the one hand, to the acquisition of qualitative differences distinguishing one rudiment from another, and, on the other hand, to their independent—in certain respects—development in the course of the ontogenesis. The specific differentiation of some rudiments has been studied by me in a number of marine and sweet-water molluscs at early stages of their development by means of determining the differential sensitivity of the individual sections of the embryo to the action of toxic substances, and their ability to reduce the oxidation-reduction indicators during intravital staining.

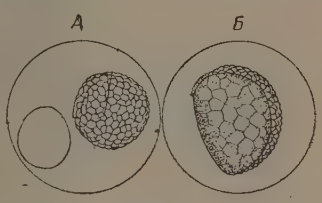

Fig. 1.

In my experiments with *Anodonta anatina* L., the results of which are described in the present communication, these methods made it possible to show with particular demonstrativeness the physiological unhomogeneity of the embryos, already at the very earliest stages of their development.

By placing *Anodonta* embryos extracted from the branchial cavity of the animal into a concentrated brilliant-cresol-blue solution, it proved possible to follow the sequence of the arising injuries caused by the action of the stain, and the dying off of individual sections of the embryo.

At the stage of 4 blastomeres, the blastomere *D* which is distinguishable in *Anodonta* owing to its large size is the first to be injured. This injury is quite clearly manifested in the experiments with brilliant-cresol-blue and it may be detected at its very beginning by the change of the tint and discoloration of the injured sections of the embryo. The blastomeres of the other quadrants are injured but considerably later and therefore remain coloured for a longer time. It was found by similar experiments that at the stage of 8 blastomeres the macromere 1 *D* possesses a relatively high sensitivity to the action of the injurious agent. At the stage of 16 blastomeres it is the so-called somatoblast 2 *d* (distinguished by its large size in the *Lamellibronchiates* and particularly large in *Unionidae*) which is electively injured. The rest of the cells show no sensitivity differences at this stage of development.

The injured blastomeres become, as a rule, more or less isolated from the rest. Experiments with the reduction of indicators under anaerobic conditions show that the blastomeres which manifest a high sensitivity, reduce the stain at a slower rate than the others.

The blastomere 2*d*, according to Lilly ([2]), produces in its subsequent development in *Unionidae*, like in other *Lamellibranchiates*, a definite section of the ectoderm which forms the conch-gland and the flittering field—the organ which provides for the rotatory motion of the developing embryo within the egg-capsule.

It is consequently possible with the help of the differential sensitivity method to establish, that a definite embryonic rudiment differs sharply from the other sections of the embryo from the physiological point of view, and to follow the transfer of the material of this rudiment at early stages of development. In experiments with oocytes taken from the gonad it was found, that the vegetative part of these cells possesses a relatively higher sensitivity. This fact may be apparently explained by the polar situation of the material of the rudiment of the conch-gland and flittering field in the vegetative area of the oocyte, which is changed only when the egg divides. Pictures of differential injury, quite analogous to those obtained in the experiments with embryos injured by placing them into a brilliant-cresol-blue solutions, were observed by me also in *Anodonta* embryos exposed to various conditions in the aquarium (overcrowding, contamination of the water by products of metabolism, etc.)

In such cases I observed at the early stages of development, i. e. at the stages of 4, 8 and particularly of 16 blastomeres, similarly to what was observed in the experiments just described, an isolation of the injured cells from the rest of the blastomeres, forming an integral complex.

Of particular interest are the anomalies in the development of the glochidia at later stages of embryogenesis proceeding under unfavourable conditions.

Sometimes one finds an animal, in which a considerable part (up to 50%) of the larvae developing in the branchial cavities prove to be defectuous. These larvae differ from the normal ones by the absence of the conch-gland and of the flittering field; due to this, they do not rotate within the egg-capsule, like normal larvae do. In other respects the defectuous glochidia prove normal and do not lag behind in the rate of their development. Many defectuous larvae, having reached a definite stage of development, show muscular mobility.

In those cases, when the developing embryo shows the above-described anomalies, we regularly find within the cocoon, in which they are developing, one or several large sized half-destroyed dead cells, completely isolated from the living embryo.

Comparing these findings with our observations on the differential sensitivity during the early stages of development which have been described above, we are fully justified in assuming that these half-destroyed and isolated cells are none other than the blastomeres of the quadrant *D*, which produce in the case of normal development the conch-gland and the flittering field and in these cases have suffered some injury and been isolated at the early stages of blastulation.

In those cases when the defectuous larva possesses muscular mobility, it seems highly probable that the injury and isolation of the blastomeres have occured after the formation of the somatoblast 2*d*, since at the earlier stages the rudiments of the conch-gland, the flittering field and the mesoderm lie in one and the same blastomere.

If, besides a defectuous larva possessing muscular mobility, the egg-capsule contains only one destroyed cell, we have grounds to consider this

cell to be the somatoblast 2*d* which has been injured in the beginning of blastulation at the stage of 16 blastomeres.

The experiments and observations described above prove the strict determinateness of a definite embryonic rudiment in the *Anodonta* and the absence of regulation in the development of this form.

While in the classic experiments of Wilson ([1]) and in those of later research-workers the determinateness of rudiments was proved with the help of mechanical separation of individual blastomeres or of their complexes from one another, in our case we reach the same conclusion on the ground of experiments with the differential sensitivity to the influence of injuring agents. The method which we employ in this case to make evident the early determination of the rudiment of the conch-gland and flittering field throws light simultaneously on some physiological features of this rudiment at the earliest stages of development.

The rudiment of the conch-gland and the flittering field, besides its relatively high sensitivity to the action of toxic substances, shows a lower capacity to reduce the oxidation-reduction indicators in experiments with asphyxia. In connexion with the early determination of the rudiments and with the physiological specificity acquired by them, their sensitivity to the action of toxic substances and to the reduction of stains show a conspicuously mosaic character. No gradualness in the spatial distribution of this sensitivity and of the capacity to reduce the indicators is observed in the embryo. In this respect *Anodonta* embryos present an instance of mosaic development and differ sharply from the embryos showing a regulatory type of development, in which Child and his school have established the presence of axial gradients for the various physiological indices.

Assuming that the axial gradients play the rôle of integrating systems at early stages of development, one can believe that in animals with a mosaic type of development the gradients can no more be detected at the egg-cell stage in connexion with the relative autonomy in the development of individual rudiments.

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CYTOGENETICS

PRODUCTION OF POLYPLOID PLANTS FROM LEAVES TREATED WITH COLCHICINE

By M. S. NAVASHIN and HELEN GERASSIMOVA

(Communicated by N. I. Vavilov, Member of the Academy, 22. VII. 1939)

Everyone who has worked on production of polyploids with the aid of colchicine treatment of the upper part of the plant knows how easily the developing leaves respond to this drug and acquire the characteristic features of polyploids: dark-green coloration, thickening, rough or crimped surface, etc. No less familiar, too, is, of course, the discomforting fact that these characters which are so clearly expressed at the beginning fade out as the plant develops and gradually disappear, so that the shoot which develops from the colchicine treated bud (be it even the first bud of the youngest seedling) proves to be an ordinary diploid. Success seems to depend on a mere accident and in certain plant species no polyploids could be so far obtained by treating vegetative organs. However, this method of obtaining polyploids is of special interest as it is the only applicable to vegetatively propagated plants where polyploid is most promising from practical point of view; the same is, of course, true of the doubling of the chromosome set in sterile hybrids for making them fertile.

As shown by our studies (the paper concerning this item has to appear subsequently in this Journal), this situation in the first place should depend on the difficulty of penetration of colchicine when applied from outside, i. e. when it is attempted to force it against the natural flow of substances. In case greater dosage is applied, the outer tissues suffer fatal changes before the drug affects enough the inner ones. Direct cytological analysis has shown that the result depends just on the above circumstance, not on preferential survival of diploid tissues (which seems to be probable at first sight; see the paper referred to above).

The above situation has naturally attracted our attention to a search for a method for direct use of the polyploid tissues which are so abundant in the leaves of treated plants. In case it were possible to grow plants from polyploid leaves, mass production of polyploids in a number of plant species would be an extremely easy affair. The interest for such a method is the greater, as the leaves are in general subject to great hereditary variation and must, therefore, give many aberrant forms (this is known from the practice of vegetative propagation); finally, it should form a unique means for analyzing chimeral plants, for studying changes occurring in ontogenesis, etc.

The great majority of plants has not been studied in respect to the possibility of obtaining regenerates from their leaves; this is especially true of

the annuals. Preliminary experiments were conducted by us in 1938; as a result it proved to be possible to root the leaves even of such annual herbs as *Crepis*. This year we attempted to obtain polyploid plants in the rubber-yielding dandelion, *Taraxacum kok-saghyz*, by means of inducing regeneration of leaves of plants previously treated with colchicine.

The first experiments yielded positive results: a large proportion of leaves formed roots 15—20 days after they were cut off and planted into sand. The leaves which formed roots were then planted into soil, where they deve-

Fig. 1.

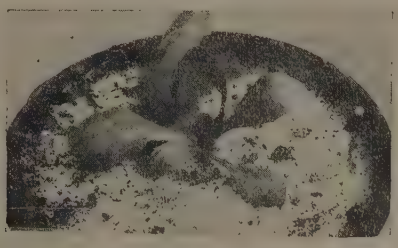

Fig. 2.

Fig. 1. Regeneration from a rooted leaf of *Taraxacum kok-saghyz*. The young rosette of leaves is developing at the base of the one of the roots formed by the old leaf (seen at the background). Enlarged about twice.

Fig. 2. Same, a few days later. The young plant has considerably developed, the old leaf is still alive. Natural size.

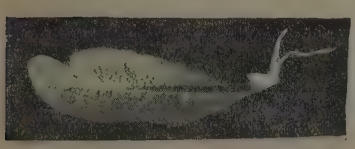

Fig. 3.

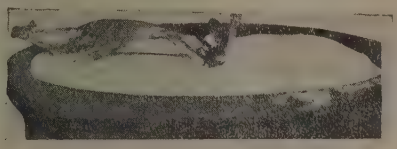

Fig. 4.

Fig. 3. A rooted leaf of a plant (39Б 1126-1) treated with colchicine solution. The right half of the leaf displays a marked primary effect of colchicine; it has formed a thick root which upon cytological investigation proved to be tetraploid. The left half of the leaf remained unaffected and has developed a thinner diploid root. Natural size.

Fig. 4. Same, 20 days later. Regeneration has begun; at the base of the tetraploid root (on the right) is developing a more vigorous (clearly tetraploid) shoot. The old leaves begin to die. Natural size.

loped a large root system; they assimilated very well, became dark-green, thick and even rolled up as a result of hypertrophy. About a month following cutting off (i. e. 15 days after the roots were formed) regeneration has begun; a little bud developed at the base of the one of the roots (Fig. 1). The bud rapidly developed so that in a few days there was a young little plant possessing a nice rosette of leaves; only the old leaf which stuck at one side reminded of its origin (Fig. 2). At the age of two months plants that had regenerated from leaves were very vigorous and were ahead of their «sibs» grown of seed. Curiously enough, the petiole of the old leaf which remained viable over a long period of time, could subsequently form additional buds which developed into new rosettes of leaves.

This method was at once applied to leaves of plants treated with colchicine and gave, as will be seen later, positive results. One instance will be described here.

A leaf of a plant treated with colchicine was cut off and rooted in sand. One could judge by its appearance (Fig. 3) that one of its sides was normal, the other—polyploid. It has developed 2 roots, one of which was thick and came out of the alleged polyploid half, the other, produced by the normal half, was thinner; the tips of the two roots were fixed for cytological examination and the leaf was planted into soil; its decapitated roots soon began to branch there.

Cytological investigation has shown in full accord with expectation that the thicker root was tetraploid (32 chromosomes), while the thinner one was diploid (16 chromosomes).

Seven days following planting of the leaf into soil regeneration began first at the base of the diploid root, and three days later at the base of the tetraploid one there arose a whole group of buds (Fig. 4). At the present time the development of the young plants is progressing quite normally, so that there is no doubt that within a month a healthy tetraploid plant will be obtained.

We have applied now the new method to the production of polyploids to a greater scale in order to obtain this autumn many polyploid plants developed from leaves which would be otherwise lost in vain.

It should be remarked that success depends on the following conditions: 1) Leaves and plants from which they are taken should not be old. 2) The wound surface should be carefully washed before planting the leaf (it is especially important in the case of *Taraxacum kok-saghyz*, as it is covered here with a water resistant membrane of rubber). 3) Leaves planted into sand should be kept out of direct sun-rays. 4) Immediately upon development of the roots the leaves should be transplanted into soil where they should be allowed to develop great roots during 4—5 days. Then the base of the petiole should be freed from soil so as to denude slightly the roots (this is better done with a jet of water).

The method worked out by us is, of course, applicable to full extent only in the case of those plants whose leaves are capable of regeneration (it should be noted parenthetically that they are probably much more common than one might think). It is especially suited for plants which form adventitious buds on their roots (kok-saghyz belongs here). Our method is of interest, too, for those plants whose leaves produce only roots without ever regenerating into new plants; it may serve to analyze cytologically any part of a shoot under application of the root-tips, i. e. of the most favourable material.

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PLANT PHYSIOLOGY

ASSIMILATION OF RADIOACTIVE ELEMENTS BY PLANTS

By V. I. BARANOV

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The influence of radioactive elements upon growth and development of plants has been tested in numerous experiments. No clear-cut evidence, however, has been produced concerning the two principal questions, very important for the practical use of those elements as fertilizers.

1. What dose is most favourable for the various crops and is it possible to substitute one element for another?

2. To what extent are the various elements taken up by the plants from the nutrient medium?

The present work is an attempt to interprete the results of some experiments on growing various cultivated plants in the nutrient media added with radioactive elements. These experiments were carried on in 1936—1938 at the Biogeochemical Laboratory of the Academy of Sciences of USSR and at the Laboratory of D. N. Prianishnikov in Timiriazev Agricultural Academy collectively*.

Pisum sativum was the chief experimental material along with *Lactuca sativa*, *Cucumis sativus*, *Linum usitatissimum* and *Avena sativa*. The plants were grown in water and sand cultures, in glass vessels containing Hellriegel's nutrient medium added with boron. This was the background which served as control. The radioactive elements added to it in varying concentrations were Ra, U and Ac. Four parallel vessels were as rule apportioned to each of the concentrations.

The question as to the behaviour of plants in response to two different elements, isotopes of Ra and Th, supplied simultaneously, was attacked in 1938 by an experiment with *Lactuca sativa* grown in one-litre porcelain beaker with a similar nutrient water solution added with the following amounts of a Ra—MsTh (I+II)—RdTh preparation (Table 1).

Table 1

		Per vessel, g	%		Per vessel, g	%
Exp. 1	Ra	$5.4 \cdot 10^{-10}$	$5.4 \cdot 10^{-11}$	RdTh	$5.27 \cdot 10^{-14}$	$5.27 \cdot 10^{-15}$
Exp. 2	Ra	$3.05 \cdot 10^{-8}$	$3.05 \cdot 10^{-9}$	RdTh	$5.8 \cdot 10^{-12}$	$5.8 \cdot 10^{-13}$

* The details concerning the method used and the data obtained are given elsewhere.

The plants when they had completed development were taken out of the vessels, weighed and tested in the laboratory.

The influence of the radioelements on plant's development was estimated by A. A. Drobkov (Laboratory of Prianishnikov), while their distribution in the plant was studied by K. G. Kunasheva and V. I. Baranov (Biogeochemical Laboratory). The radioactivity was measured for the aerial organs and the root system separately.

In the tests of 1936 the optimal concentrations for the development of plants were as follows (Table 2).

Table 2

Exp.	Time	Culture	Radioelement	Optimal concentration, %
1	23.V—11.VII	*Pisum sativum*	Uranium	$8.5 \cdot 10^{-6}$
2	23.V—11.VII	*Pisum sativum*	Radium	$1.7 \cdot 10^{-12}$
3	23.V—11.VII	*Pisum sativum*	Actinium	$6.0 \cdot 10^{-15}$

For comparing the radioactive energies corresponding to the optimal doses we must take into consideration the radioactive constants of the respective radioelements (Table 3).

Table 3

Water culture	Radioelement	Half-life period, years	Optimal concentration		
			%	Atoms decaying in 100 cm^3 per min.	Ratio to the average
Pisum sativum	Ra	$1.59 \cdot 10^9$	$1.7 \cdot 10^{-12}$	3.8	1.0
» »	Ac with its decay products . . .	13.5	$6.0 \cdot 10^{-15}$	1.6	0.42
» »	U free from Ra .	$4.4 \cdot 10^9$	$8.3 \cdot 10^{-6}$	6.1	1.6
			Average	3.8	

From these data it will be obvious that the optimal concentration of the radioelements tested in the nutrient medium, expressed in % by weight, varies up to 10^9 times. If, however, the values of optimal concentration are multiplied respectively by decay constants and the magnitudes proportional to the number of atoms decaying in unit time are considered, all the values obtained for different radioelements will be very close to each other and the ratio of variation will be only 1 to 4. It should be noted thereby that those values of optimal concentration are correct only within the order of magnitude. For the other crops tested in water medium the optimal concentration of radium are of the same order of magnitude*.

The conclusion to be drawn is that the optimal concentrations of various radioelements in the nutrient medium correspond to a nearly equal number of atoms decaying in unit time, i. e. lie close to the energy of the atomic decay. In other words, the optimal concentrations are equiradioactive.

* In sand cultures better results were obtained by Drobkov with a 10 times higher concentration of Ra, i. e. $n \cdot 10^{-11}$%. By its order of magnitude this concentration of Ra approaches to that in natural soils.

Absorption of Radioelements by Plants. The experiments on the uptake of radioelements by the plants grown on radioactive nutrient media gave the following results (Table 4).

Table 4

Uptake of Ra by *Pisum sativum*

			%	$2.42 \cdot 10^{-13}$	$2.42 \cdot 10^{-12}$	$2.88 \cdot 10^{-11}$	$2.42 \cdot 10^{-10}$
	In the nutrient medium		Atoms decayed in 100 cm^3 per min.	0.54	5.4	64	540
Concentration of Ra	In the plant with respect to the medium	Aerial organs		20	0.82	1.17	2.1
		Roots		42.5	60	50.5	45
		Aerial organs + + roots . .		30	8.4	8.4	9.4

Uptake of Ac by *Pisum sativum* *

			%	$9.6 \cdot 10^{-16}$	$9.6 \cdot 10^{-15}$	$9.6 \cdot 10^{-14}$	$9.6 \cdot 10^{-13}$
	In the nutrient medium		Atoms decayed in 100 cm^3 per min.	0.25	2.5	25	250
Concentration of Ac	In the plant with respect to the medium	Aerial organs		—	—	6.9	19.4
		Roots		2 960	396	920	1 780
		Aerial organs + + roots . .		273	47.5	100	211

Uptake of Ra and RdTh by *Lactuca sativa*

Radioelement				Ra		Rdth	
			%	$5.4 \cdot 10^{-11}$	$3.05 \cdot 10^{-9}$	$5.3 \cdot 10^{-15}$	$5.8 \cdot 10^{-13}$
	In the nutrient medium		Atoms decayed in 100 cm^3 per min.	121	6 800	9.8	1 070
Concentration of radioelements	In the plant with respect to the medium	Aerial organs		0.39	0.025	0.33	0.012
		Roots . . .		17.1	51.4	26.4	45.7
		Sum		3.55	8.0	7.1	7.1

The data referred to enable us to the following conclusions:

1. In all cases the concentration of radioelements calculated on the live weight basis proved to be higher in the plant than in the nutrient medium:

* Data on actinium uptake by plants have been obtained for the first.

Uptake of Ra by *Avena sativa* and *Linum usitatissimum* in Response to Varying Doses

	In the nutrient medium		%	$2 \cdot 10^{-12}$	$2 \cdot 10^{-10}$	$2 \cdot 10^{-8}$
			Atoms decayed in 100 cm³ per min.	4.46	446	44 600
Concentration of Ra	In the plant with respect to the medium	Aerial organs	*Avena sat.*	6	2.25	0.22
			Linum usit.	25	1.1	0.17
		Roots	*Avena sat.*	280	320	110
			Linum usit.	230	60	240

16.3 times for Ra in peas; 5.8 times for Ra in lettuce; 7.1 times for RdTh in lettuce and 160 times for Ac in peas. The experiments of 1936 and 1937 are in good agreement. A striking feature to note here is that actinium is to a much higher extent concentrated by the plants compared to the other radioelements tested.

2. The concentration of radioelements in the aerial organs is well below that in the root system, the difference being as high as two orders of magnitude for all of the elements tested.

3. Where the lettuce plants had been given 10—100 times higher doses of Ra and RdTh compared to the optimal ones, the concentration of both of those elements in the aerial organs calculated with respect to the concentration in the nutrient medium was 10 times less than with optimal doses. The relative concentration in the roots was not changed appreciably. Similar results were obtained by Kunasheva in the experiment of 1938 with other crops (flax and oats).

This gives us grounds to suppose that the radioelements are not so easily taken up by the plants if supplied in high concentrations, owing probably to their radioactivity.

4. The supposition is confirmed by the fact that the Ac which emitts no appreciable radiation is taken up by the plants in higher concentrations than the other radioelements (with reference to its concentration in the nutrient medium).

5. Of utmost importance for the practical use of radioactive fertilizers is the circumstance that the different radioelements applied in optimal doses exhibit a similar radioactive energy and that the optimal doses for the development of different plants are of the same order of magnitude. It appears therefore possible in a number of cases to substitute one radioactive element with another taken in equiradioactive amounts. We have also to point out here that the optimal dose of Ac was obtained for a preparation of Ac in a state of equilibrium with RdAc and AcX and refers to those latter elements rather than to Ac itself.

It stands to reason that the above conclusions need further verification by experiments on other crops and nutrient media. The next problem to be studied is the absorption by plants of various radioactive isotopes within a wide range of relative radioactivity. This problem is of great theoretical interest and also very promising from the practical point of view. As a particular case we can meet here with considerable disturbance of the radioactive equilibrium in plants considered with regard to the nutrient medium. Another important point is further to study the distribution of radioelements in various parts and organs of plants as well as to test the action of α, β and γ-rays emitted by the radioelements.

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EXPERIMENTAL MORPHOLOGY

EFFECT OF THE CORTEX OF SUPRARENALS ON THE SEXUAL APPARATUS. II. GONADOTROPIC ACTION OF THE SUPRARENAL CORTEX OF MAN

By V. R. KLIACHKO

(Communicated by I. I. Schmalhausen, Member of the Academy, 17. VII. 1939)

In the first part of this work we reported on the early sexual maturity occurring in infantile rats and mice under the influence of suprarenal cortex extracts of cattle and pig. An investigation of the gonadotropic substance of the human suprarenal cortex seemed to us of particular interest, since it is known that early sexual development is sometimes observed in children showing hyperfunction of the suprarenal cortex, for instance, in patients with cortex tumors. Besides, this substance has so far not been investigated in man.

Experiments Involving the Administration of the Extract of Human Suprarenal Cortex. Suprarenals of human persons were obtained in acetone from the Department of Pathological Anatomy of the Sklifassovsky Institute. Suprarenal glands of adults of both sexes, who had perished mainly from traumas, were taken for these experiments. Those of children and aged persons were not investigated. At various dates eight lots of suprarenal glands were treated, each of them including from 4 to 50 glands.

Introduction of the Extract to Infantile Female Rats. The extract was tested on 41 infantile rats, varying in weight between 30 and 40 g; 0.5—1.0 cm^3 of the extract was injected 3 times daily for 2 days. The dosage of the extract varied from 10 to 500 mg of «alcoholic» powder, these amounts being equivalent to 1—45 g of the suprarenal

Table 1

Treatment with Extract of Human Suprarenal Cortex

	Number of animals	Variation in weight of ovaria in mg	Average weight of ovaria in mg	Variation in weight of uterus in mg	Average weight of uterus in mg
Control rats	30	7—14	10	20—40	27
Rats under test	27	13—22	16	77—241	99
Control mice	20	2—3	2.4	7—11	9
Mice under test	6	3—5	4.2	14—26	19

Note. The data refer to an oestrus provoking dosage.

gland respectively, if the average weight of a human suprarenal is taken to be 12 g. After the opening of the vagina, vaginal smears were taken from every rat and examined (Table 1).

100—120 hours after the first injection the rats were sacrificed. Their ovaria and uteri were weighed and fixed for histological examination. The thyroid glands of these rats and occasionally their uterus as well were subjected to histological examination, too. As controls served the group of infantile rats (Fig. 1) previously used by us for comparison with the test rats treated with cattle or pig suprarenal cortex extract (cf. Communication I). Moreover, in some experiments conducted on rats of the same litter, one rat

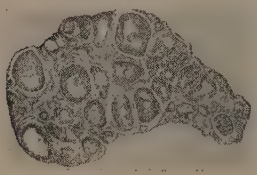

Fig. 1. Ovarium of a control rat, × 27.

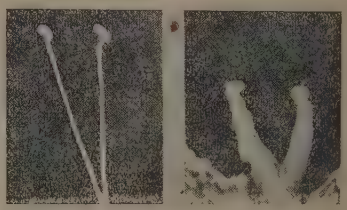

Fig. 2. Treatment with human suprarenal cortex extract. Uterus and ovaria of two rats from the same litter (left, control; right, experiment): Natural size.

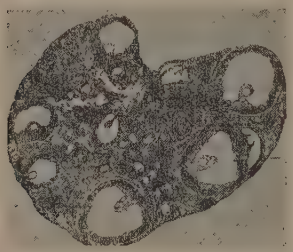

Fig. 3. Ovarium of a rat treated with human suprarenal cortex extract. Killed 100 hours after injection. Large mature follicles visible. × 27.

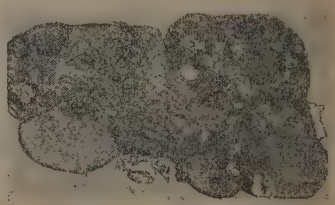

Fig. 4. Ovarium of rat treated with human suprarenal cortex extract. Killed 120 hours after injection. Two corpora lutea visible. × 27.

from every litter received injections of the solvent used in the extract and served as control.

Results of the Experiments. Under the influence of human suprarenal cortex extract the rats under test showed disclosure of the vagina and oestrus. The weight of the ovaria of the rats at the time of oestrus or metaoestrus varied between 13 and 22 mg, the average thus equalizing 16 mg.

The weight of the uteri varied between 47 and 241 mg, the average being 99 mg [the maximum weight of the ovaria of control rats was 14 mg, that of the uteri 40 mg (Table 1 and Fig. 2)]. Histological examination of the ovaria showed the presence of large-sized mature follicles with big cavities (Fig. 3); some of the ovaria contained corpora lutea (Fig. 4). In the uteri we found typical oestral and metaoestral alterations. The histological picture of the thyroids was approximately similar in both control and test animals.

The experiment described above showed that 1 kg of human suprarenals (assuming their average weight to be 12 g) contained from 22 to

Control Male Rats

No.	Weight of rat in g	Weight of seminal vesicles in mg	Weight of prostate in mg	Weight total in mg	Weight of testicles in mg
1	50	12	40	52	300
2	63	16	41	57	599
3	54	16	31	47	509
4	47	15	23	38	345
5	47	14	28	42	329
6	48	16	34	50	355
7	54	17	34	51	264
8	54	17	41	58	452
9	48	16	33	49	492
10	50	19	33	52	669
11	59	11	36	47	407
12	50	19	34	53	769
13	56	—	—	52	715
14	58	11	31	42	355
15	53	12	33	45	412
16	56	14	35	49	426
17	49	13	35	48	431
18	49	15	36	51	452
19	57	18	41	59	582
20	54	17	30	47	528
21	61	19	32	51	608
22	60	18	30	48	622
23	52	14	36	50	502
24	54	17	29	46	564
25	49	15	42	57	386
26	58	16	36	52	582
27	53	12	33	45	613
28	54	11	37	48	337
29	48	11	39	50	361
30	56	—	—	46	771
31	52	—	—	44	612
32	50	13	47	60	406
33	58	14	28	42	508
34	49	11	32	43	362
35	52	14	48	52	384
36	54	12	40	52	412
37*	49	15	48	63	317

Weight of seminal vesicles from 11 to 19 mg

Weight of prostate . . . . . from 23 to 48 mg

Weight of seminal vesicles and prostate . . . . . from 38 to 63 mg

Weight of testicles from 264 to 771 mg

* Rat from the progeny of the set in which the extract from the man's suprarenal cortex was introduced.

Table 2

Introduction of Prolane to Male Rats

No.	Weight of rat at the end of the test	Dose of prolane in rat unit	Weight of seminal vesicles in mg	Weight of prostate in mg	Weight total in mg	Weight of testicles in mg
1	51	2	—	—	—	309
2	49	2	22	54	76	473
3	52	4	24	91	115	352
4	52	4	22	105	127	408
5	49	8	25	125	150	368

Experiment lasted 5 days.

Introduction of the Extract from the Suprarenal Cortex of Cattle to Male Rats

No.	Weight of rat at the end of the test	Dose of extract in rat units	Weight of seminal vesicles in mg	Weight of prostate in mg	Weight total in mg	Weight of testicles in mg
1	46	2	16	52	68	482
2	48	2	17	43	60	325
3	52	2	22	49	71	412
4	49	2	—	—	88	512

Experiment lasted 5 days.

Introduction of Extract from Suprarenal Cortex of Man to Male Rats

No.	Weight of rat at the end of the test	Dose of extract in rat units	Weight of seminal vesicles in mg	Weight of prostate in mg	Weight total in mg	Weight of testicles in mg
1	47	2	28	92	120	355
2	48	2	30	86	116	371
3	47	2	29	102	131	330
4	47	3	30	112	142	386

Experiment lasted 10 days.

1 000 rat units of gonadotropic substances, possessing both a follicle stimulating and a luteinizing effect. The least content in gonadotropic substances was shown by those lots of suprarenals which were composed of glands taken not only from persons who had perished of traumas, but also from patients who had died of other causes. One lot, consisting only of suprarenals of patients who had died of various chronic diseases (encephalitis, sepsis, etc.), contained no gonadotropic substances. In a part of the rats which had been treated with human suprarenal cortex extract, we tested the gonadotropic activity of the hypophysis; this was found, however, to differ but little in control and experimental rats.

Administration of the Extract to Infantile Mice. The test was done on 10 mice weighing 6—8 g each. The doses of the extract varied between 1.2 and 2 rat units. As controls served the lot of infantile mice previously used for comparison with mice treated with cattle suprarenal cortex extract (cf. Communication I).

Results of the Experiment. Doses containing 1—2 rat units resulted in the disclosure of the vagina and oestrus (in 2 cases there was no pure desquamation stage). The weight of the ovaria of the mice at the time of oestrus varied between 3 and 5 mg, that of the uterus between 14 and 26 mg [the highest weight of the ovaria in the controls equalized 3 mg, that of the uterus 11 mg (Table 1)]. Histological examination showed the presence of maturing follicles, with a big follicular cavity, in the ovaria; one of the ovaria contained a corpus luteum. «Blutpünkte» failed to be found in any of the cases. The picture of the uterus corresponded to the phase of the sexual cycle.

Administration of Human and Cattle Suprarenal Cortex Extracts to Male Infantile Rats. The control group of rats consisted of 37 animals weighing from 47 to 63 g each. In the control animals we weighed out both testes, seminal vesicles and prostates; after this they were fixed for histological examination. As the chief criterion of the activity of the extracts tested was taken the weight of the seminal vesicles and prostates. The weight of the testes could not be taken as such a criterion, since it was found to vary greatly in the control animals (from 264 to 771 mg). Moreover, it is known that the seminal vesicles and prostates respond readily to the introduction of even small quantities of gonadotropic substances, while great amounts of these substances are necessary to stimulate the testes. The total weight of the seminal vesicles and prostate varied in the control animals between 38 and 63 mg. 3 lots of rats were injected gonadotropic substances: to the 1st lot we administered prolan (for sake of comparison), to the 2nd—cattle suprarenal cortex extract, to the 3rd lot composed of rats of the same litter aged 22 days—human suprarenal cortex extract. To the first two lots injections were continued for 5 days, to the third one for ten days. The results of the experiment are summarized in Table 2.

Extract from cattle suprarenal cortex provoked but a slight stimulation of the genitalia, the total weight of seminal vesicles and prostate varying between 68 and 88 mg. A much more pronounced stimulation was obtained by means of human suprarenal cortex extract. In this case the total weight of seminal vesicles and prostate varied between 116 and 142 mg. It was difficult to detect any histological differences between the prostates and seminal vesicles of the test and control animals, since both these organs had already reached a considerable degree of development in the controls. The only difference noticed was that the epithelium of the seminal vesicles was higher in the test animals than in the controls. The histological picture of the testes was also similar in both groups.

Conclusions. 1. Human suprarenal cortex extract provoked early sexual maturity in female infantile rats and mice (disclosure of vagina, oestrus, weight increase of uterus and ovaria, rapid maturing of follicles and formation of corpora lutea).

2. Human suprarenal cortex extract provoked a weight increase of the prostate and seminal vesicles in male infantile rats.

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